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METALS RECOVERY FROM INDUSTRIAL SLUDGES

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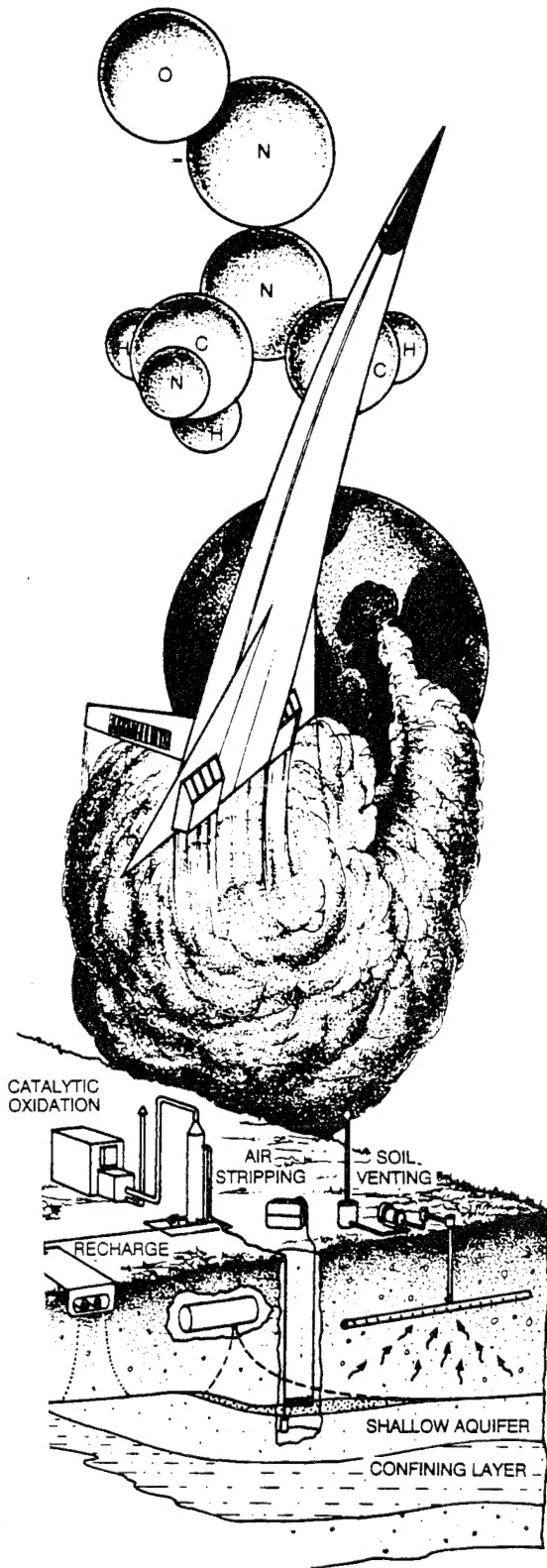
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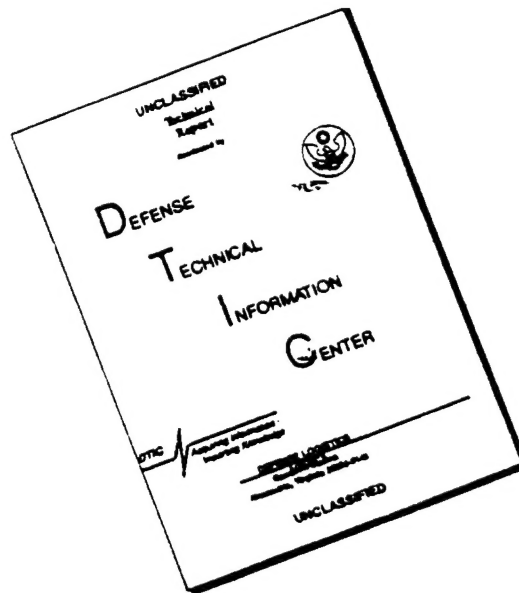


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13. ABSTRACT (Maximum 200 words) This report describes the Metals Recovery from Industrial Sludge Program. The program objective is to identify or develop processes for reclaiming metals from a mixed, metal-bearing, waste sludge produced by the Industrial Waste Treatment Plant at Tinker AFB and other facilities where similar waste treatment processes are used. A literature review, market survey, and preliminary laboratory tests have been done. Metal separations appear promising through selective chemical precipitation processes. Other technologies, including electrowinning, electro dialysis, and wet air oxidation may be combined with chemical precipitation to offer a feasible metals recovery process. A building was constructed around the Tinker AFB demonstration IWTP system during Phase I in order to offer climatic protection to the other AF projects currently being performed at this site. The Phase II program consisted of bench-scale tests of identified unit processes and a continued search for alternative treatment methods. Phase II efforts identified an overall metals recovery scheme that was subjected to bench-scale testing and generated a data base for the design of a pilot field verification unit. Phase III of the metals recovery program will consist of design, construction, and operation and evaluation of the field verification unit.				
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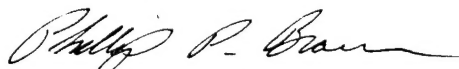
PREFACE

This report was prepared by the U.S. Department of Energy, Idaho Operations Office, EG&G Idaho Inc, P.O. Box 1625, Idaho Falls, ID 83415 under DOE Idaho Field Office Contract DE-AC07-76ID01570 for the Air Force Civil Engineering Support Agency, 139 Barnes Drive, Tyndall AFB, FL 32403-5319.

This report summarizes work completed during CY90 thru CY92 to identify methods to treat sludge generated by sodium sulfide/ferrous sulfate treatment of industrial wastewater at Tinker Air Force Base. The Air Force project officer was Lieutenant Phillip P. Brown, AFCESA/RAVS.

This report has been reviewed by the Public Affairs Officer (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for public release.



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SUMMARY

This report presents recommendations for a process to treat sludge generated by sodium sulfide/ferrous sulfate treatment of industrial wastewater at Tinker Air Force Base (AFB). The purpose of this process is to minimize hazardous residuals and to recover ferrochromium alloy for reuse. The process recommended consists of five steps: (1) sludge concentration by gravity settling, (2) chemical oxidation of the concentrated sludge with hydrogen peroxide, (3) gravity separation of the effluent from the oxidation step into liquid organic, aqueous, and sludge phases, (4) dewatering of the treated sludge, and (5) pyrometallurgical treatment of the dewatered sludge to recover ferrochromium alloy and produce nonhazardous by-products. This process is recommended based on previous laboratory- and bench-scale testing of several alternative treatment processes.

This report also provides preliminary design information for a pilot plant to evaluate, optimize, and demonstrate the first four steps of the recommended process. The pyrometallurgical process step will be demonstrated at a vendor facility off-site. The design information provided includes a design basis, process description, process flow diagram, material balance, equipment list with preliminary sizes for major equipment, and a cost estimate.

As an alternative to sludge treatment by the recommended process mentioned above, it may be possible to treat dewatered sludge directly without any other treatment in a pyrometallurgical process to recover ferrochromium alloy. While these processes typically cannot accept metal sulfide sludges containing sulfur, organic, and other contaminants which exceed maximum concentration limits, one vendor of pyrometallurgical technology will accept Tinker AFB metal sulfide sludge for testing based on the sludge characterization established in Phase I. This alternative could be evaluated by sending a sample of dewatered metal sulfide sludge from Tinker AFB to this vendor for testing. This could be done instead of the pilot-scale testing of the process described above or in parallel with the pilot-scale testing.

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LIST OF ABBREVIATIONS

AFB	Air Force Base
AFCESA	Air Force Civil Engineering Support Agency
ALC	Air Logistics Command
APT	Advanced Processing Technologies, Inc.
ASH	Air-Sparged Hydrocyclone system
CEC	cation exchange capacity
COD	chemical oxygen demand
CRU	chromium reduction unit
EDTA	ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
ICP	inductively coupled plasma
INEL	Idaho National Engineering Laboratory
IWTP	Industrial Wastewater Treatment Plant
KAX	potassium amyl xanthate
MIBC	methyl isobutyl carbinol
mgd	million gallons per day
MSDS	Material Safety Data Sheet
NPDES	National Pollutant Discharge Elimination System
SBH	sodium borohydride
SBS	sodium bisulfite
SCC	Solids Contact Clarifier
TAFB	Tinker Air Force Base
TCLP	toxicity characterization leaching procedure
TGSCC	transgranular stress corrosion cracking
USBM	U.S. Bureau of Mines
WAO	Wet-Air Oxidation
XRD	X-Ray diffraction

SECTION I INTRODUCTION

The Air Force Civil Engineering Support Agency (AFCESA) has sponsored development work at Tinker Air Force Base (AFB) in Oklahoma City, Oklahoma, to reduce the amount of hazardous waste generated by the Air Logistics Command (ALC) processes. The Industrial Wastewater Treatment Plant (IWTP) at Tinker AFB currently treats wastewaters from electroplating (degreasing, alkaline cleaning, electrocleaning, acidizing, and depositing protective metals electrochemically), engine cleaning, and paint-stripping processes. A research and development program was initiated by the United States Air Force to treat these wastewaters to meet federal and local environmental regulations by removing and recovering the heavy metals.

Efforts on Phase I of this project were reported by Suciu (Reference 1). In summary, the report stated, "The overall conclusion of this project is that the selectivity of the metal separation that was desired is not achievable with the technology and conditions tested." Because of the lack of positive results from the efforts noted in Reference 2, new directions (Phase II) were developed for the FY 90 research and development effort. The results of the FY 90 efforts were reported by Ugaki (Reference 2), and from this effort came the recommendation that additional work be undertaken for the FY 91 research and development effort, constituting Phases II and III.

As a continuation of the development of the sodium sulfide/ferrous sulfate treatment process, the AFCESA has sponsored further effort to investigate removal of heavy metals from the hazardous sludge and produce residuals that are nonhazardous. This effort includes a feasibility study of available technologies, laboratory- and bench-scale testing (Phase II, Task 3), field pilot-scale testing (Phase III, Task 5), and a field demonstration of the process with the field pilot-scale unit.

The work reported here was conducted by the Idaho National Engineering Laboratory (INEL) through the U.S. Department of Energy, Idaho Field Office, at the INEL Research Center for the U.S. Air Force. The results of the research and

development program described in this report are detailed in Section III, C, Task 3. Section III, D, provides the results of Task 4, i.e., the economic evaluation of a proposed pilot plant for treating the Solids Contact Clarifier (SCC) underflow sludge. Section IV provides the pilot plant design.

Subsequent to the initiation of Phase I of the study, a point source reclamation program was put into operation at Tinker AFB, which significantly reduced the amount of metals entering the IWTP. While the heavy metal content of the water is still above the levels allowed for discharge under present and future National Pollutant Discharge Elimination System (NPDES) discharge limits, the quantity and nature of the sludge produced by the sulfide/sulfate treatment process has changed. Consequently, the requirements for treating and recovering metals from this sludge differ from those described previously.

A. OBJECTIVE

The objectives of this phase of the metals recovery project are to develop, test, optimize, and demonstrate a process to remove, and recover for reuse, heavy metals from the industrial sludge generated by the sodium sulfide/ferrous sulfate treatment of wastewater at the IWTP at Tinker AFB. The process developed will, to the extent possible, maximize the recovery of metals in the sludge for reuse, produce nonhazardous by-products, and minimize the volume of hazardous residuals. The reclaiming process shall not have an adverse impact on the operation of the IWTP or the quality of effluent discharged from this facility.

B. BACKGROUND

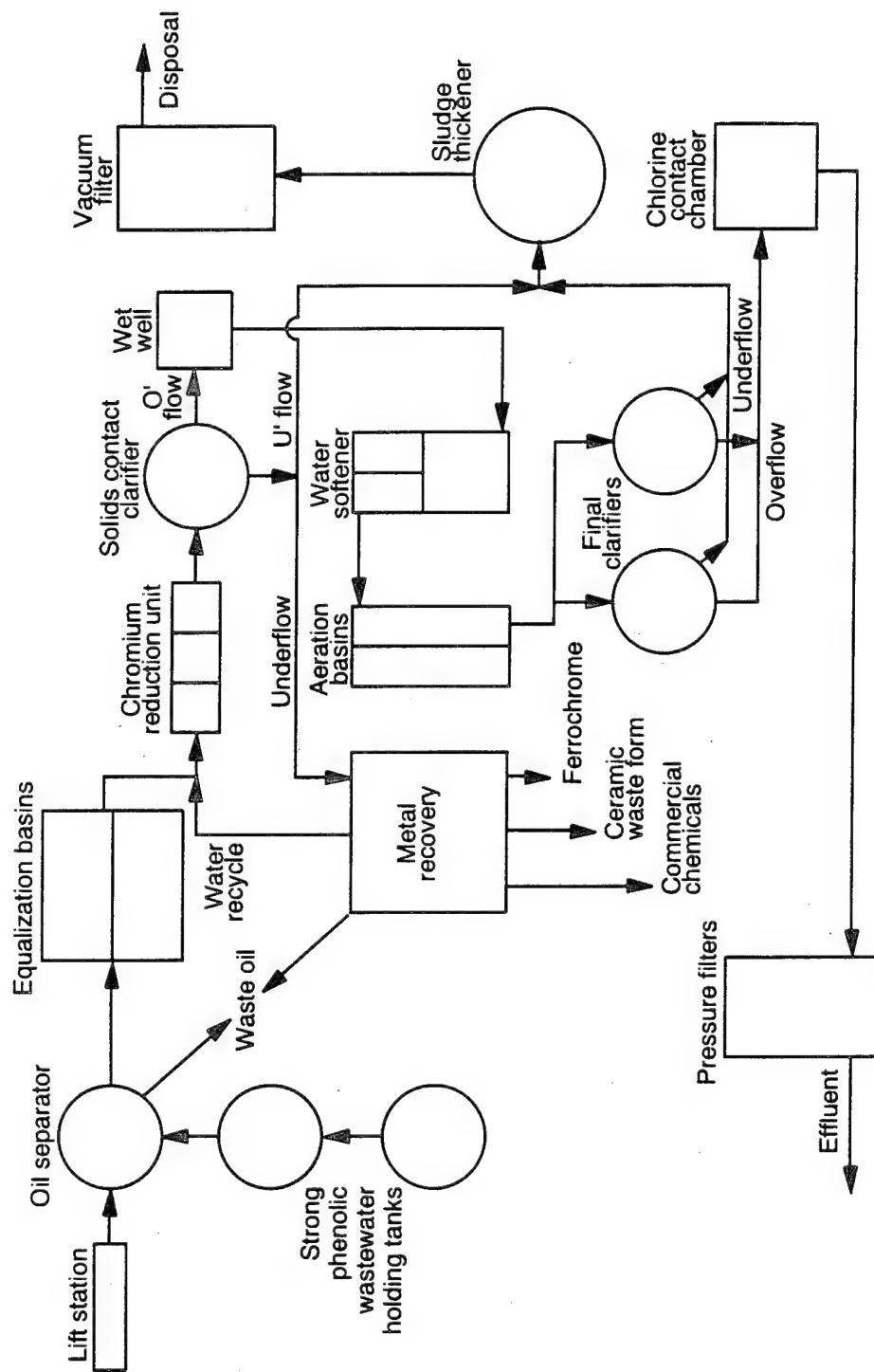
The IWTP at Tinker AFB treats 0.5 to 1.3 million gallons per day, approximately 0.7 million gallons per day, of wastewater daily producing between eight to nine tons of sludge per day. This sludge is approximately 0.3 to 8 weight percent solids and is comprised of biological sludge from the activated sludge system and metal-bearing sludge from the IWTP Solids Contact Clarifier (SCC). The biological sludge contributes six to seven tons per day to the mixture, with the remaining one to two tons coming from the metal-bearing sludge that is the underflow of the SCC. The biological and metal-bearing sludges are

combined in a thickener tank. The sludges produced from these wastes are classified as Environmental Protection Agency (EPA) F006 wastes, which are defined by the EPA as wastewater treatment sludges from electroplating operations, except for certain defined processes (Reference 3). These wastes are hazardous because of the metal and sulfide contents and require special handling and costly disposal (as much as \$700/barrel in 1991)* in approved hazardous waste repositories. Also, the composition of the incoming waste stream is not constant but depends on the nature of daily aircraft-refurbishing operations at Tinker AFB.

The Tinker AFB aircraft-refurbishing and maintenance operations include degreasing, alkaline cleaning, electrocleaning, acidizing, electrochemical deposition of protective metals, engine cleaning, and paint stripping. These operations produce waste streams containing oils and greases; metal ions; and complexing and chelating agents such as tartrates, phosphates, cyanide, ethylenediaminetetraacetic acid (EDTA), and ammonia (Reference 4). The hazardous metals include cadmium, chromium, copper, silver, lead, nickel, and zinc. The aqueous mixed-waste streams are typically treated in multiple stages. These stages include destroying cyanide, skimming off oils and greases, reducing hexavalent chromium to trivalent chromium, precipitating metals, and degrading remaining organics by passing the remaining waste stream through an activated sludge system (Reference 3). This effluent is then filtered and released to the environment. A schematic flow diagram is presented in Figure 1.

The metal-bearing waste sludge is generated by the reduction of hexavalent chromium to trivalent chromium and subsequent precipitation of heavy metals with the addition of sodium sulfide and ferrous sulfate at near neutral to slightly alkaline conditions to avoid generation of hydrogen sulfide. This process has maintained the effluent from the IWTP at Tinker AFB within the NPDES permit requirements (Reference 5) when properly operated. Some of the NPDES metal constituent limits are listed in Table 1.

* Private communication from R. L. Miller to V. L. Capps, Information for Metals Recovery Tasks 4 and 5, RLM-45-91, October 9, 1991.



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Figure 1. Process Flow Diagram, IWTP, Tinker AFB.

TABLE 1. TINKER AFB NPDES PERMIT REQUIREMENTS.

Constituent	Effluent Limit		Concentration, December 1992 (mg/L)	
	Concentration, Before August 1988 (mg/L)	Concentration, After August 1988 (mg/L)	Acute	Chronic
Cadmium, total	0.03	0.015	0.074	0.002
Chromium, total	1.0	0.1		0.05
Chromium, hexavalent	0.1	0.1		0.022
Copper, total	0.1	0.05	0.037	0.023
Lead, total	0.1	0.05	0.197	0.008
Nickel, total	1.0	0.5	2.55	0.283
Zinc, total	1.0	0.5	0.211	0.191

C. APPROACH/SCOPE

The phases and tasks comprising the "Validation of Metals Recovery from Industrial Sludges" project are described in Section II of this report. The thrust of this report are Tasks 3, 4, and 5, described in Section II.

The approach to the Chemical Leaching and Precipitation Studies, as described in Task 3 in the following section, is to review the prior efforts and the literature to identify what appeared to be the best available technologies for treatment of the type of sludge obtained from the SCC, and to determine the physical and chemical characteristics of the sludge. (Tasks 1 and 2 were reported previously, Reference 1). This information provided a basis for the test design. This report presents information obtained from literature, the several approaches used for solid-liquid separation, the procedures employed to treat the sludge to facilitate metal separation, the results of metal separation efforts, and the results of experiments to reduce the remaining solids to an innocuous, nonleachable, nontoxic waste form. Also included in this report are appendices describing procedures used for the experiments and the conclusions and recommendations.

SECTION II

PROGRAM DESCRIPTION

The program consists of three phases. In the scoping study performed in FY 89, a literature search and market survey, physical characteristic studies, biological leaching studies, chemical leaching studies, and various metal recovery techniques were examined. The following is a description of the scope of the three program phases.

A. PHASE I: LITERATURE SEARCH/MARKET SURVEY AND PRELIMINARY LABORATORY STUDIES

1. Task 1: Literature Search/Market Survey

The recommendations of the scoping study (Reference 1) suggest that chemical precipitation, smelting to obtain a ferrochromium product, ion exchange, and combinations of these technologies are the most promising metals recovery options. An additional literature review was conducted to determine the extent, availability, and applicability of these processes. The option of identifying commercial reclaimers capable of accepting and processing the metal-bearing sludge was explored in a market survey.

2. Task 2: Sludge Characterization Studies

The initial characterization of the sludge in the scoping studies was inadequate for metals separation and recovery process identification. Analytical methods have been developed for determining the metals content of the sludge, extractable organics in the sludge, and dry solids content for the thickened metal-bearing sludge and vacuum-filtered wet sludge cake. These methods were used for sludge characterization.

3. Task 3: Chemical Leaching and Precipitation Studies

The sequential dissolution method proposed in the scoping studies for selectively extracting individual metals from the metal-bearing sludge was

evaluated.- This method incorporated the ability of selected leaching solutions to preferentially remove specific metals from the metal-bearing sludge. Additionally, studies were performed to determine the most effective leaching solution for complete dissolution of the sludges in preparation for chemical precipitation separations.

4. Task 4: Other Metal Recovery Studies

Other technologies identified in Task 1 were explored further. These technologies included electrodialysis, wet-air oxidation, and electrowinning.

5. Task 5: Construction of Building Around Tinker AFB Field Demonstration IWTP System

A portable building has been erected around the Tinker AFB field demonstration IWTP system. The building is equipped with all of the environmental controls necessary to conduct research and to permit operation of the field demonstration unit throughout the year without interruption due to weather conditions.

B. PHASE II: PROCESS OPTIMIZATION/FIELD DEMONSTRATION DESIGN

The following quotations are from the Statement of Work from the funding authorization document.*

"Phase II will consist of bench-scale testing of identified unit processes and a continued search for alternative methods. At the end of Phase II an overall metals recovery scheme will have been identified and subjected to bench-scale testing and a data base generation for the design of a pilot field verification unit."

* Military Interdepartment Purchase Request No. N91-25, "Validation of Metals Recovery from Sludges," dated December 12, 1990.

1. Task 1: Completion of Phase I Reports

"Two reports are in progress. A draft report, "Metals Recovery from Industrial Sludges," was issued for review and comment in January 1990. A second report, on work accomplished in FY 90, is in progress. A draft of this report will be distributed for review and comment. Comments will be resolved and the final reports submitted to the Air Force Engineering and Services Center."

2. Task 2: Revise Cost Account Plan and Program Strategy

"A revised Cost Account Plan for this program is to be prepared and issued in December 1990. This revised plan will identify a detailed schedule of the work to be accomplished in FY 91 and is to include additional testing of alternate metal recovery schemes. The revised plan will include any changes made necessary by the previous year's research."

3. Task 3: Continue Laboratory and Bench-Scale Dynamic Testing

"Laboratory testing is required to further define a process that will operate effectively on the material designated for effective metals recovery. Bench scale tests will continue to be conducted to determine the effect of continuous operation on the efficiency of metal recovery from each unit process. Each unit process and operation will be tested for compatibility with the 'total process.' A total process will be selected, based on feasibility, compatibility, and economics. Included in this task are efforts on sludge characterization, test plan preparation, and safety analysis for both the Idaho Falls and Tinker AFB laboratories and test facilities. The process will be evaluated for compliance with state and federal regulations."

4. Task 4: Process Economic Evaluation and Regulatory Analysis

"The process(es) selected for metals recovery will be subjected to economic analysis to determine viability as a method for sludge treatment."

C. PHASE III: FIELD DEMONSTRATION TESTING

"Phase III of the metals recovery program will consist of design, construction, and operation and evaluation of the pilot field verification unit. This phase will begin in FY 92." However, economic considerations may limit application of the technology derived from the present research and development.

1. Task 5: Completion of Field Engineering Design

"The Field Demonstration Unit will be designed to accomplish the metals recovery required by this program. The design is to be based on the results of Task 3. Sufficient detail will be provided for modification of the existing field demonstration unit to permit integration of the metals recovery system into the facility at Tinker AFB. A final report on the results of laboratory testing, process selection, and economics will be prepared."

2. Task 6: Procurement of Materials and Components

"Procurement shall be initiated for long lead materials and components that will be needed to construct the pilot field verification unit. Initiation of this task shall be conducted in a timely manner to eliminate delays in construction and operation of this unit."

3. Task 7: Construction of a Pilot Field Verification Unit

"A site will be prepared for construction of the field demonstration unit at Tinker AFB. The field demonstration unit is to be constructed and integrated into the existing field demonstration facility at Tinker AFB. The unit is to consist of all unit processes and operations selected for optimal metal recovery from the sludge produced by the sodium sulfide/ferrous sulfate process."

4. Task 8: Operation of the Pilot Field Verification Unit

"The field demonstration unit will to be used to optimize each of the processes with respect to concentration, flow rate, temperature, etc. As each step is optimized, it is anticipated that some previous steps may require modifications. Following optimization, the pilot plant process is to be operated continuously for a period of time to determine the impact of continuous operation and changes in the sludge on the overall process. The resulting data generation will provide sufficient information to completely design, construct, and operate a system at the IWTP for recovery of heavy metals from the Tinker AFB industrial effluent."

5. Task 9: Preliminary Economics of the Process

"The economic analysis will include disposition costs or salvage value of the final product from the metal recovery system in the system's recommended configuration. The analysis will evaluate the unit operations and unit processes and apply appropriate costs for construction and continuous operation. The analysis will consider all of the necessary regulatory requirements for discharge, transportation, etc. of the materials involved."

6. Task 10: Final Report Preparation

"A final report on the operation of the metals recovery field demonstration unit will be prepared and will include the operating ranges found for the system and the interaction of the metals recovery system on overall field demonstration operation. Further, the report will include all environmental and economical information necessary to determine whether or not to implement full-scale recovery operations. The report will contain all the necessary data and information from all of the listed tasks which are necessary to support the conclusions. This report will contain the necessary data to design, construct, and maintain a full-scale system."

SECTION III
PHASE II RESULTS

A. TASK 1: COMPLETION OF PHASE I REPORTS

The draft report, "Metals Recovery from Industrial Sludges," (Reference 1) was issued for review and comment in January 1990. This review was completed, the report was issued, and is listed as Reference 1 in this report. A second report on work accomplished in FY 90 was issued for review and comment in January 1991. This review was completed, the report was issued, and is listed as Reference 2 in this report.

B. TASK 2: REVISE COST ACCOUNT PLAN AND PROGRAM STRATEGY

A revised Cost Account Plan was prepared and issued. This revised plan identified a detailed schedule for the work to be accomplished in FY 91 and included additional testing of alternate metal recovery schemes. The revised plan included any changes made necessary by the previous year's research and changes in the waste stream due to point source treatment.

C. TASK 3: CONTINUE LABORATORY AND BENCH-SCALE DYNAMIC TESTING

The industrial wastewater, including plating wastes, is treated in the IWTP. The nominal inflow to the IWTP is about 0.7 million gallons per day but varies from about 0.5 to 1.5 million gallons per day (Reference 6). The influent has a chromium concentration of about 1 milligram/liter and other toxic metals are present at lower concentrations. Even after application of point source treatment procedures, the concentrations of heavy metals still exceed the discharge limits for the IWTP, as given in Table 1. Determination of the most effective methods for recovering the metals in the sludge from the IWTP is the thrust of the present study.

The influent water is treated for removal of floating hydrocarbons, but this treatment is only suitable for removal of a portion of the floating organic phase as it leaves a small amount of the hydrocarbons in suspension or in

solution. This water is then treated with sodium sulfide and ferrous sulfate to reduce the Cr^{+6} to Cr^{+3} and to form precipitates of metal oxides/hydroxides and metal sulfides. Cationic and anionic polymers are then added to coalesce the fine particles produced by this procedure and to improve sedimentation in a Solids Contact Clarifier. The SCC is described in Reference 3. The overflow from the SCC averages about 0.7 million gallons per day and contains a small amount of the heavy metals as sulfide "pin floc" which escape the coalescence/sedimentation process. This overflow is sent to an activated sludge digester for further treatment. The SCC underflow is about 5000 gpd, or about 0.7 percent of the IWTP throughput and has a pH of 7.2 to 7.5. The heavy metals content of the sludge is determined by the solubility of the various compounds. The suspended and dissolved oil and grease in the sludge coats the precipitated particles. Sedimentation tests show that some of these particles float while others settle, indicating significant differences in specific gravity of the particles, which is due to the coating of oil and grease and entrained gases. Treatment of the SCC underflow to recover the toxic metals is the subject of the present study; removal of the hydrocarbons entrained in the solids is a secondary benefit.

1. Solid-Liquid Separation Studies

The costs for disposal of the hazardous waste generated by treatment of the IWTP influent are based on weight. The disposal cost is high (presently as much as \$700/drum or \$3100/ton)* and will likely increase substantially. Even before point source treatment facilities were installed, nearly all of the weight of the waste consisted of water. The solids content of the SCC underflow (including the organics) originally ranged from 1 to 3 percent (Reference 1) but has declined to <0.5 percent after application of point source treatment. Very significant savings in disposal costs would accrue if a highly efficient scheme was devised for separation of toxic solids from the otherwise innocuous liquid from the SCC underflow. Filtering processes fare poorly with sulfide sludges because of the fine particle sizes and, especially in this case, because of the

* Unpublished communication from R. L. Miller to V. L. Capps, Information for Metals Recovery Tasks 4 and 5, RLM-45-91, October 9, 1991.

organic coatings and the polymers used to assist agglomerating and settling. Since filtering was shown to be ineffective, alternative solid-liquid separation techniques were investigated to achieve this objective, with froth flotation and gravity separation approaches receiving the most emphasis.

a. Froth Flotation of Sludge

Froth flotation has been used routinely to treat oil-contaminated waste waters and is often the preferred technology for separating oil from tanker ballast, from oil well production waters, and from waste waters of a variety of oil processing facilities (References 7 and 8). Because of the oil coating on the Tinker AFB sulfide sludge particles it was thought that the solids in this sludge might be naturally floatable; that is, merely injecting air would enable a separation of the solids. This was found to be the case; however, the addition of methyl isobutyl carbinol (MIBC) improved recovery.

Froth flotation is used also to treat significant quantities of copper, phosphate, and iron ores, as well as to reduce the sulfur content of coal (Reference 9). A "collector" is used to improve separation efficiency. In the case of the copper sulfide ores, which constitute the greatest tonnage treated by flotation, a collector is used which has an affinity for sulfide surfaces and which forms a coating to enable a firm attachment of the bubbles so that the sulfide particles may be floated more easily. The sulfide-collector combinations exhibit surfaces similar to those found on the oil-coated metal sulfide particles that are the subject of this study. Xanthates are used most often as collectors for sulfide ores; potassium amyl xanthate (KAX) was used in this study. This collector has little or no affinity for oxides, chlorides, carbonates, etc., so these materials are not floated.

Frothers are added so that bubbles are formed readily and will persist for a time period sufficient for separation to be effected. Air is introduced into the flotation cell and dispersed by an impeller, as are the small ore particles, to produce an agitated mixture of a large number of fine bubbles and ore particles for maximum opportunity for contact. Separation occurs when the bubbles, with the particles attached, spill over the side of the flotation

cell into the launder. A properly selected frother will enable the bubbles to persist long enough for the froth to be swept into the launder. The froth should then collapse and release the particles so that a "foam breaker" will not be required. Frequently used frothers are the petroleum-base blends, followed by aliphatic alcohols (Reference 9), such as MIBC.

Nine flotation tests were made on the Tinker AFB sludge. These tests were run by Advanced Processing Technologies, Inc. (APT). In the first eight tests, the as-received slurry was used to produce two rougher concentrates that were collected after each run. The variations in conditions for Tests 1 through 8 are summarized in Table 2 and conditions for Test 9 are given in Table 3. The procedures used for conducting these tests are detailed in Appendix A. Visual observation showed that using the MIBC frother resulted in a more uniform bubble size of about 1 to 2 centimeters in diameter. When MIBC was not used, the bubble sizes were observed to vary considerably, with diameters up to 4 centimeters. Use of the MIBC frother also improved water rejection into the tailings. The results of Tests 1-8 are shown in Table 4.

Test 1 was conducted to determine the extent of natural floatability of the sludge, so no collector or frother was added for this test. When air was admitted, bubbles formed on the sludge and immediately confirmed the speculation that this oil-bearing metal sulfide sludge would be naturally floatable. The bubbles were large, some being in the range of 4 centimeters, with 2 centimeter bubbles being common. Large bubbles are unstable and difficult to sweep from the cell into the launder.

Test 2 was performed to determine the effect of adding 25 milligrams per liter of MIBC to the sludge. No collector was added in this test. When air was admitted, the froth formed on the slurry and the first flotation concentrate was collected. An additional 25 milligrams per liter of MIBC was added to the sludge prior to collecting the second flotation concentrate. The bubbles were about 1 to 2 centimeters in diameter, which is typical of many flotation froths. The solids recovery was better in Test 2 than in Test 1. These results suggest that the addition of MIBC does not improve water rejection but does improve solids recovery by about 3 percent. Test 2

protocol was used as the basis for comparing the results of the follow-on tests, with variables limited to the addition of collectors and modifying agents. The high concentration of MIBC used in Test 2 was designed to simulate the frother requirements for APT's Air-Sparged Hydrocyclone. This unit requires a higher frother concentration to maintain the taller froth column as compared to the froth column in conventional froth flotation cells. See Table 2 test data. Because of potential problems from MIBC in the water recycled to the IWTP, a frother will not be used for froth flotation.

KAX was used in Test 3 as the collector at a dosage of 25 milligrams per liter for the first flotation concentrate and an additional 5 milligrams per liter for the second flotation concentrate. MIBC frother was added to a concentration of 25 milligrams per liter. The froth was similar in appearance to that obtained during Test 2. This test protocol was designed to provide maximum water rejection rather than maximum solids recovery; however, both improved solids recovery and water rejection were achieved.

In Test 4, no collector was added to determine the overall effect of oxidizing the sludge during flotation. MIBC was added to a concentration of 25 milligrams per liter. Two grams of potassium monopersulfate were added to the cell during conditioning to oxidize the sulfide particles, at least on their surfaces, so that only the oil would be floated. The results were inconclusive and both solids recovery and water rejection were decreased by this treatment. Other conditions for this test were similar to Test 2. When air was admitted, the froth formed on the pulp. The bubbles were mostly uniform in size and about 1 centimeter in diameter.

Polymers were added to the sludges in Tests 5 through 8 to see if solids recovery and water rejection could be improved. Betz Industrial* polymers 1195, a cationic polymer, and 1125, an anionic polymer, were used to promote agglomeration and settling in the SCC; these polymers were already present in the sludge solids and, thus, were not added in this series of

* A division of Betz Laboratories, Inc.

TABLE 2. FROTH FLOTATION INPUT CONDITIONS, TESTS 1 THROUGH 8.

Test No.	First Rougher Concentrate				Second Rougher Concentrate		
	Collector		Added concentration mg/L	Frother concentration mg MIBC/L	Flotation Time min	Collector added concentration mg/L	Frother concentration mg MIBC/L
	Name						
1	None	0	0	1	1	0	5
2	None	0	25	1	1	0	25
3	Potassium Amyl Xanthate	25	25	1	1	5	25
4	Potassium Mono-Persulfate	2000	25	1	1	0	25
5	Betz Polymer 1175	10	25	1	1	0	25
6	Betz Polymer 1190	10	25	1	1	0	25
7	Betz Polymer 1180	10	25	1	1	0	25
8	Betz Polymer 1180	25	25	1	1	0	25

TABLE 3. EROTH FLOTATION DATA FOR TEST 9.

	Frother Addition	Flotation Time	
Stage No.	mg MIBC/L	Min/Stage	Cumulative
1	25	1.0	1.0
2	0	1.0	2.0
3	0	1.5	3.5
4	0	2.0	5.5
5	0	3.0	8.5

TABLE 4. RESULTS OF TESTS 1-8 FOR THE FOAM FLOTATION OF SOLIDS FROM AN OIL-BEARING METAL SULFIDE SLUDGE.

	Test Number							
	1	2	3	4	5	6	7	8
1st Flotation Concentrate								
Time, min	--	3.0	3.0	3.0	1.0	1.0	1.0	1.0
Pulp, g	52.0	151.3	55.2	77.5	66.5	66.1	55.7	59.9
Solids, g (dry)	2.2	2.2	2.6	2.2	2.3	2.5	2.2	2.4
Solids, percent	4.23	1.45	4.7	2.8	3.5	3.8	3.9	4.0
Solids Distribution	66.7	63.0	68.0	54.0	66.0	64.0	51.0	69.0
Water Rejection, percent	95.0	85.0	94.0	92.0	93.0	93.0	94.0	94.0
2nd Flotation Concentrate								
Time, min	--	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Pulp, g	60.6	89.0	44.2	45.0	48.3	52.3	58.8	32.3
Solids, g (dry)	0.9	1.2	1.0	0.7	1.1	0.8	1.4	0.6
Solids, percent	1.48	1.34	2.3	1.6	2.3	1.5	2.4	1.9
Solids Distribution	27.3	34.0	26.0	17.0	31.0	20.0	33.0	17.0
Water Rejection, percent	94.0	90.0	95.0	95.0	95.0	94.0	94.0	97.0
Combined Concentrate								
Pulp, g	112.6	240.3	99.4	122.5	114.8	118.3	114.5	92.2
Solids, g (dry)	3.1	3.4	3.6	2.9	3.4	3.3	3.6	3.0

TABLE 4. RESULTS OF TESTS 1-8 FOR THE FOAM FLOTATION OF SOLIDS FROM AN OIL-BEARING METAL SULFIDE SLUDGE.

	Test Number							
	1	2	3	4	5	6	7	8
Solids, percent	2.75	1.41	3.6	2.4	3.0	2.8	3.2	3.3
Solids Distribution, percent	93.9	97.0	95.0	71.0	94.0	85.0	84.0	86.0
Water Rejection, percent	89.0	76.0	90.0	88.0	86.0	88.0	86.0	91.0
Tailings								
Solids, g (dry)	0.2	0.1	0.2	1.2	0.1	0.6	0.7	0.5
Solids, percent	0.02	0.01	0.02	0.14	0.01	0.07	0.08	0.55
Solids Distribution, percent	6.1	3.0	5.0	29.0	3.0	15.0	16.0	14.0
Computed Head								
Solids, g (dry)	3.3	3.5	3.8	4.1	3.5	3.9	4.3	3.5
Solids, percent	0.33	0.35	0.38	0.41	0.35	0.39	0.43	0.35
Solids Distribution, percent	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

experiments. The Betz technical representative recommended that other Betz polymers, noted below, could be effective in improving the efficiency of flotation and were used in Tests 5 through 8.

In Test 5, Betz polymer 1175 was added to attain a concentration of 10 milligrams per liter in the pulp and 25 milligrams per liter of MIBC was added as a frothing agent. This is a strong cationic polymer used for improving oil/water separations, including applications in froth flotation of oily wastewaters. The bubbles were mostly uniform in size and about 1 centimeter in diameter. Solids recovery was about the same as that obtained in Test 2. However, the water rejection was about 5 percent better than that achieved for Test 2.

In Test 6, Betz Polymer 1190 was added to attain a concentration of 10 milligrams per liter in the pulp and 25 milligrams per liter of MIBC was added as a frothing agent. This polymer is a strongly cationic, low-molecular-weight coagulant that promotes clean separations of oil and water in froth flotation systems. The polymer is resistant to chlorine and for this reason its use may not be beneficial in follow-on unit processes. The bubbles were mostly 1 to 2 centimeters in diameter. Solids recovery was about 1 percent less than that achieved for Test 2. Water rejection was similar to that for Test 5, i.e., about 4 percent better than that achieved for Test 2.

In Test 7, Betz Polymer 1180 was added to attain a concentration of 10 milligrams per liter in the pulp and 25 milligrams per liter of MIBC was added as a frothing agent. This is another strongly cationic polymer used for making oil/water separations, including separation in froth flotation systems. The bubbles formed were mostly uniform in size and about 1 to 2 centimeters in diameter. Solids recovery was the same as that achieved for Test 2.

In Test 8, Betz Polymer 1180 concentration was increased to 20 milligrams per liter in the pulp and 25 milligrams per liter of MIBC was added as a frothing agent. The bubbles were mostly uniform in size and about

1 centimeter diameter. Solids recovery was about 5.2 percent better than that achieved for Test 2.

In Test 9, the concentrated slurry was treated with MIBC to attain a concentration of 25 milligrams per liter in the first stage; no additional frother was added and no collector was used. After conditioning for one minute, air was admitted to the cell and the flotation concentrates were collected. Input conditions and flotation times for Test 9 are shown in Table 3. The results are given in Table 5.

In summary, Test 1 showed that the sludge is naturally floated and neither frother nor collector are necessary to make a good solids separation from the sludge. Test 2 showed that a frother improved both solids recovery and water rejection. Test 3 included both a frother and a collector and this combination resulted in the best recovery and water rejection. Tests 4 through 8 included an oxidizer or polymers, but no advantage was gained by these additions. Because the solids are readily floated, an economic analysis will be required to justify the use of a frother or a collector in the system.

If water carryover is too high, the use of a second flotation circuit for cleaning the concentrate from the first system may be desirable. A flotation system using four cells for making the first concentrate and a two-cell system for cleaning the concentrate is shown in Figure 2.

(1) Conclusions from Froth Flotation Studies

The conclusion from the tests reported here is that froth flotation is a viable unit operation for processing the SCC underflow from the Tinker AFB IWTP. The tests show that in the absence of added flotation reagents, 90 percent of the sludge solids were floated and 90 percent of the water was rejected. The addition of 25 milligrams per liter of methyl isobutyl carbinol gives better water rejection and represents the base line data for comparison with other tests. Because of potential operational and environmental problems in pilot plant operation, the decision was made to not use a frother during flotation.

TABLE 5. FROTH FLOTATION RESULTS FOR TEST 9.

	Flotation time (min)	Concentrate pulp (grams)	Dry concentrate (grams)	Concentrate solids (percent)	Solids distribution (percent)	Water rejection (percent)
1 Rougher Concentrate	1.0	134.4	5.3	3.9	22.0	87
2 Rougher Concentrate	1.0	173.8	7.5	4.3	32	80
3 Rougher Concentrate	1.5	120.9	5.6	4.6	24	83
4 Rougher Concentrate	2.0	93.9	3.5	3.7	15	84
5 Rougher Concentrate	3.0	29.3	0.7	2.4	3	94
Combined Concentrate Tailings			22.6 1.1	5	95	49
Computed Head				2.37	100	

Note: This test was made using 5 drops of MIBC for stage 1. The feed was pulp filtered from 8 liters of as-received feed and re-pulped to 1.0 liters for flotation. Stopping the flotation at 3.5 minutes would yield 57 percent water rejection with 78 percent solids recovery.

The addition of potassium amyl xanthate, a commonly used collector for sulfide minerals, did not result in significant improvement of the flotation process.

The addition of potassium monopersulfate, an oxidizing agent, to the flotation slurry resulted in a lower solids recovery and is not recommended.

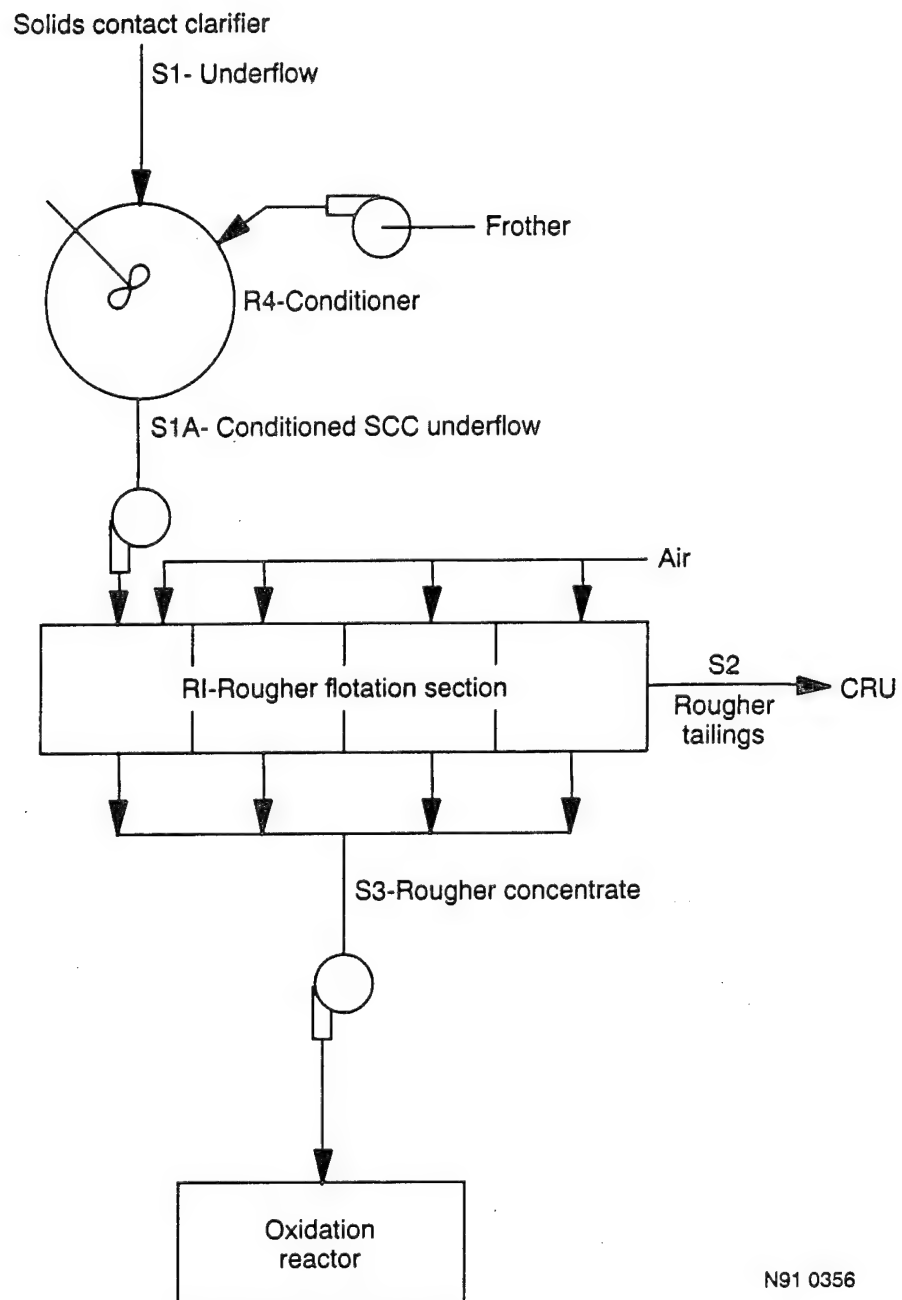
The addition of polymers as collectors for the oil as suggested by a major froth flotation system builder and by a major supplier of polymers, did not result in significant improvements in solids recovery.

The addition of flotation reagents to the SCC underflow would produce an additional burden on the activated sludge digester. These reagents should be avoided in view of the small improvements obtained in solids recovery and water rejection.

The tests by Advanced Processing Technologies, Inc., were designed to identify probable feed conditions for their Air-Sparged Hydrocyclone system (ASH). The test results appear to support a belief that the ASH system might be a viable option for upgrading the solids content of the underflow from the SCC and provide a better feed for treatment in follow-on unit processes. However, the ASH flotation system is not amenable to batch testing procedures. Further, units smaller than 3 inches have been found to be unstable during operation, and flow rates less than about three gallons per minute are not suitable in the 3-inch unit. The size of the Tinker AFB sludge sample used for the flotation studies was too small to enable testing with the ASH system; however, APT personnel indicated that the test protocols used in the flotation tests reported here encompass the conditions found in their ASH cells.

(2) Recommendations from Froth Flotation Studies

The recommendation is that the sludge be treated by froth flotation with appropriate conditioning of the slurry. The use of a frother or a collector will have to be justified through an economic analysis. The flotation concentrate may then be treated by the unit processes or operations



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Figure 2. Flow Sheet for Froth Flotation of Sludge.

that will result in the generation of end products that can be recycled to the electroplating plant, sold to commercial users, or converted to a nonleachable waste form, e.g., a ceramic.

b. Filtration of SCC underflow sludge

The objective of this study is to determine the effect on filtration rate of potential treatment methods that could be used to oxidize the sulfides, oils, and greases. Specifically, this study is concerned with the precipitate that results from the hydrogen peroxide treatment of SCC underflow sludge. A comparison was made between sludges that were oxidized using the hydrogen peroxide treatment and those that were untreated.

Filtration rate tests were conducted on two samples of SCC underflow sludge and two samples of this sludge after oxidation by 1.5 percent hydrogen peroxide. The procedure for this test is given in Appendix A, Method F.

The results of these filtration tests are shown in Figure 3 which shows that sludge filtration was slightly inhibited by the oxidation, i.e., the oxidized sludge required 10 to 20 percent longer to filter than the untreated sludge. The filtration behavior of the electrochemically oxidized sludge is similar to that of the peroxide-treated sludge. The resulting average percent solids for the untreated sludges and treated sludges were 19.1 and 18.6 percent, respectively. The resulting dry masses for the two untreated aliquots were 2.20 and 2.18 grams, while the same size aliquots after treatment and drying gave 1.79 and 1.82 grams. These filtrates were not analyzed for soluble species.

(1) Conclusions and Recommendations from the
Filtration Tests

The results of the filtration tests showed that the oxidized sludge, which is mostly in the hydrous oxide form, is moderately more difficult to filter than the untreated sludge. The loss of weight upon treatment and filtration could be the result of the loss of oils. The increased solubility of the hydroxide precipitates versus the sulfide precipitates is too small, in

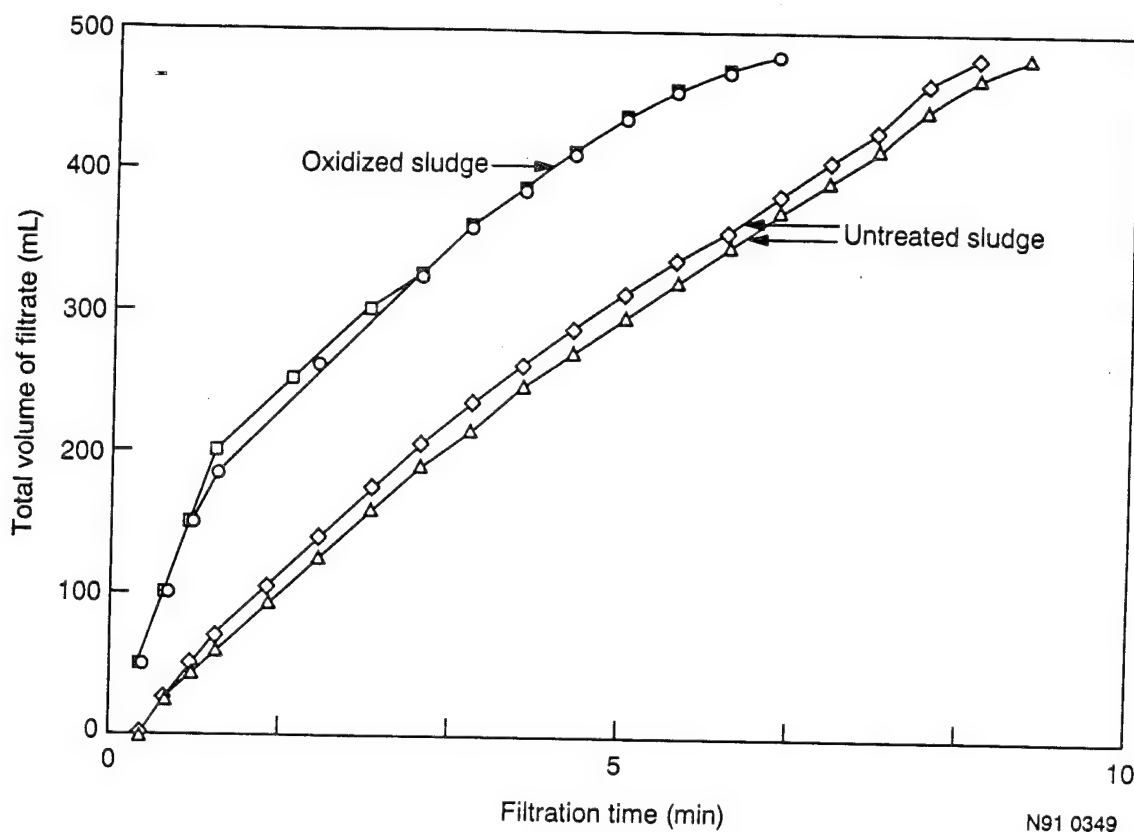


Figure 3. Results of Filtration Tests on Untreated and Oxidized Sludge.

terms of mass, to account for weight differences.

c. Sedimentation of SCC underflow sludge

Sedimentation tests were made on two samples of SCC underflow sludge that were untreated and two samples that had been oxidized with hydrogen peroxide. Procedures for these tests are given in Appendix A, Method G.

Results of the sedimentation tests, shown in Figure 4, indicate that oxidized Tinker sludge settles two to three times faster than the untreated sludge. Oxides and hydroxides have a low affinity for hydrocarbons compared to the sulfides and the oxidation process results in the release of oils and grease from the sludge solids. This loss of oil and grease upon oxidation increases the density of the sludge solids and results in more rapid settling.

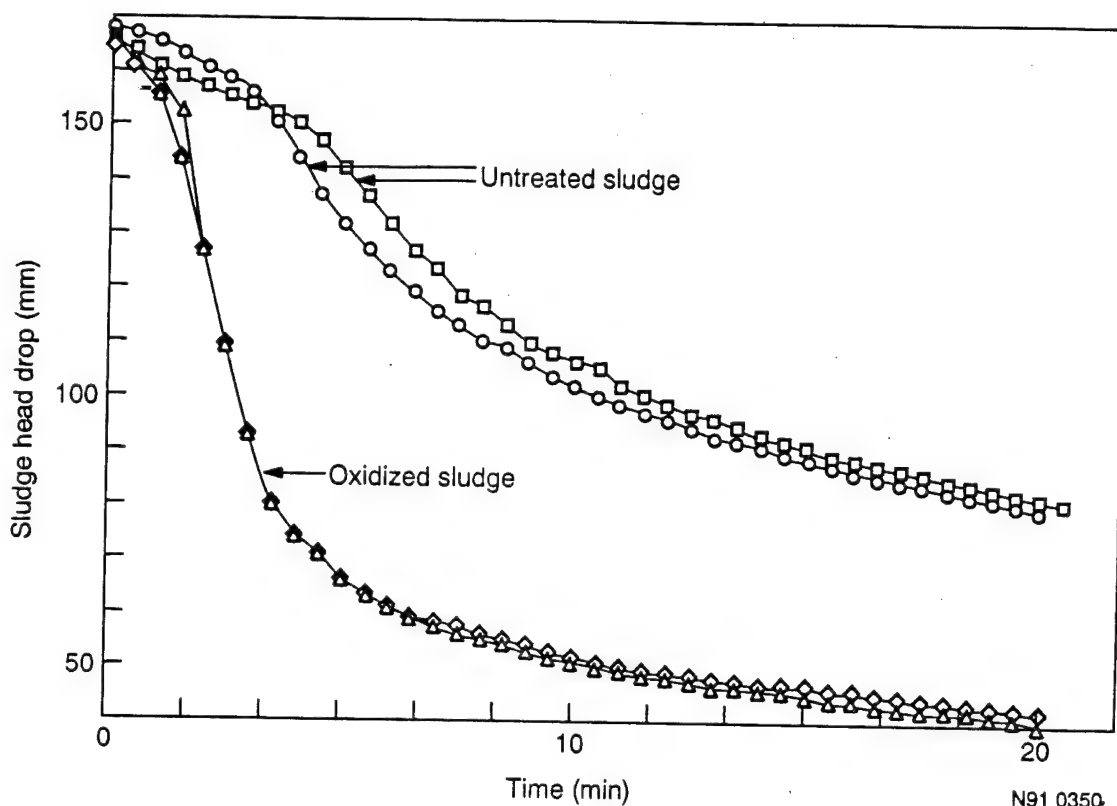


Figure 4. Results of Sedimentation Tests on Untreated and Oxidized Sludge.

(1) Conclusions and Recommendation from the Sedimentation Tests

Based on the experiments just described, one would expect that settling of 500 gallons of oxidized Tinker sludge could result in a settled sludge volume of 120 gallons after 20 minutes. This layer could then be drawn from the bottom of the settling tank and sent directly to a filter press. The settling can be performed as a batch, or as continuous flow, if the cross-sectional flow rate is kept low enough to allow sludge sedimentation to proceed.

2. Sludge Oxidation Studies

Oxidation of the sulfides in the sludge is necessary to solubilize the metals for recovery. The oxidation processes described below are carried

out with the sludge at an initial pH of 7 - 7.5; the pH may change as a result of the generation of species that will hydrolyze to form sulfuric acid, for example test conditions a relatively insoluble precipitate was formed; this contains the iron, aluminum, and chromium as oxides or hydroxides. Oxidation of the sulfide to sulfate may result in the formation of lead or barium sulfate as part of the precipitate, depending on the concentration of the metals in the sludge. Other metals, such as nickel and cadmium will be in the aqueous phase as nickel and cadmium sulfates.

With the sulfides eliminated, it is now possible to separate and recover the metals; however, for the present purpose the production of ferrochromium from the iron and chromium contained in the oxidized sludge solids is a programmatic objective of the program. Formation of a ceramic waste form (slag) from the remaining constituents in the oxide solids is also considered desirable. Recovery of the metals from the aqueous phase is feasible, but not necessarily economically practical.

Three modes of oxidation were investigated, electrochemical oxidation, hydrogen peroxide oxidation, and wet-air oxidation at high temperatures and pressures. A solids content of 1 percent is acceptable for the oxidation processes discussed here. A 0.3 percent solids sludge needs some concentration in order to reduce reagent consumption, i.e., for the same amount of reagent and sludge a low concentration of reagent will frequently yield slow and incomplete reactions. Destruction of a portion of the organic fraction of the sludge solids occurred in the case of wet-air oxidation. There was no evidence of organic phase destruction in the case of electrooxidation or hydrogen peroxide oxidation. The fate of the organic polymers, used in coagulation of the solids, is unknown.

a. Electrooxidation Processing

A process for the electrochemical oxidation of sulfide minerals was developed by the U.S. Bureau of Mines (USBM), Reno Research Center, Reno, Nevada and reported under the term electrooxidation (Reference 10). Electrooxidation relies on the in situ formation of chlorine at the anode and sodium hydroxide at the cathode. The chlorine is hydrolyzed by the water to form hypochlorous acid (HOCl) and hydrochloric acid. The hypochlorous acid is the

active species for oxidation of sulfide to sulfate. Studies at the USBM have demonstrated that the chlorine or hypochlorous acid is the active oxidizer in the process; the hypochlorite ion is slow at effecting oxidation of sulfides. Further, they found that sulfide minerals vary in their response to a chlorine environment, e.g., pyrite or iron sulfide, FeS_2 , of geological origin reacts very slowly in these environments. The iron sulfide present in the SCC underflow reacts very rapidly, probably due to its high specific surface area. The process is pH-sensitive and proceeds best under neutral to acidic conditions.

Electrooxidation has the advantage of requiring only a low-hazard chemical, e.g., sodium chloride, as input. When a direct current is applied to the electrodes in a chloride-containing metal sulfide sludge, chlorine, hypochlorous acid, and hypochlorite ions are produced. These oxidized chlorine species attack the sulfides. The relative amounts of the oxidants are pH-dependent (Reference 11).

Electrooxidation has the advantage of low reagent input, as most of the impetus for chemical changes is provided by the electrical energy, so only those reagents that enable electrooxidation to function need be added to the cell. In the case of commercial cells that generate hypochlorite, intermediate species are also generated (hydroxyl radicals, peroxides, etc.,) that will readily oxidize the sulfide sludges.

Electrooxidation results in rapid conversion of sulfides. Unpublished work on electrooxidation of sulfides in solution and freshly precipitated lead sulfide showed that the oxidation of the sulfide was essentially complete in the time of mixing. The metals present in the sludges form sulfates, hydroxides, and hydrous oxides upon electrooxidation. The sulfide species are nonpolar and capable of adsorbing large amounts of oil, while hydroxides and sulfates are polar and tend not to adsorb oils. As a result of sulfide destruction by oxidation, most of the adsorbed oil is released and is able to float to the surface. The fate of the organic polymers, added in the chromium reduction unit (CRU) to coagulate and flocculate the sulfides, is unknown. The procedures for conducting the electrooxidation tests are provided in Appendix A, Method H.

(1) Results and Discussion of Electrooxidation

Results of the duplicate analysis performed on 1 gram samples of the 10 percent reconstituted sludge are shown in Table 6. The sludge solids concentration is based on the calculated mass of solid expected for the 10 percent solids sludge. The difference between duplicate analyses was found to be on the order of 1 percent, based on the total amount of metal present. This is within the precision of the analytical method used.

The metals listed in Table 6 account for 6 percent of the solid sludge mass, with the remaining 94 percent composed of mostly oils, plus sulfate and hydroxyl anions and organic polymer bound water.

The oxidation of the sludge resulted in a limited plating of metals on the cathode. The quantity of metals plated from the resulting 5 percent solids sludge mixture after 1 hour can be found in Table 7. The metals given in Table 5 were present at approximately $3.1 \times 10^5 \mu\text{g}$ and the amount plated on the cathode was $378 \mu\text{g}$, or roughly 0.1 percent of the metals available in the solution. Although electrowinning may be attractive in terms of low chemical input, the quantity of metals plated was too low to make efficient use of electrical energy.

Analysis of the plated metals indicates that some species that would be expected to electrodeposit, e.g., mercury, are not present, while barium and aluminum which are not electroplated from aqueous solutions are present. The absence of mercury is probably due to its low concentration in the solution. The presence of barium and aluminum is attributed to occlusion of solution within or under the other plated metals. The pilot-plant electrooxidation system would probably use platinum or palladium-coated electrodes rather than graphite electrodes and the platinum or palladium electrodes would probably not adsorb as many of the metals as the graphite electrodes.

Electrodeposition of metals during electrooxidation of sulfide sludges can be expected to lower the concentration of free metals in solution during the oxidation. The soluble metal levels are given in Table 8.

TABLE 6. DUPLICATE ANALYSIS OF TINKER AFB SULFIDE SLUDGE.

<u>Metal</u>	<u>µg/g of sludge solid</u>	<u>Metal</u>	<u>µg/g of sludge solid</u>
As	57	As	28
Hg	4	Hg	6
Se	36	Se	34
Cr	29100	Cr	29100
Cd	339	Cd	342
Pb	220	Pb	213
Ni	1550	Ni	1520
Fe	22500	Fe	22600
Al	5920	Al	5500
Ba	<u>2050</u>	Ba	<u>2050</u>
Total	61800	Total	61400

TABLE 7. METALS PLATED FROM SLUDGE.

<u>Metal</u>	<u>µg plated</u>
As	0
Hg	0.13
Se	0
Cr	96.8
Cd	4.6
Pb	3.3
Ni	24.7
Fe	181
Al	27.3
Ba	<u>39.7</u>
Total	378 µg

TABLE 8. METALS IN SOLUTION AFTER OXIDATION.

<u>Metal</u>	<u>µg/mL solution</u>
As	0
Hg	0
Se	0.4
Cr	0.83
Cd	0.65
Pb	0
Ni	6.05
Fe	0.33
Al	0.29
Ba	0.78

The relatively high and nearly uniform concentration of nickel over the test period indicates the nickel sulfide initially present in the sludge solids has been solubilized by electrooxidation. All of the metals, except nickel, were found to have concentrations less than 1 part per million. While the relatively high nickel concentration may attract some interest in terms of recovering this metal from the solution by electroplating, it should be noted that, as the concentration of a metal decreases, the electroplating efficiency decreases. At nickel concentration levels where the water would meet NEPA discharge criteria, the plating efficiency would be very low and other species, such as hydrogen, would be preferentially reduced. However, recovery of nickel from wastewater or mine water by the overall process of sulfide precipitation, concentration, and recovery by electroplating may have application to recovery of this metal from low-grade sources.

Figure 5 demonstrates the current response to a potential difference of 4.0 VDC over the course of the sulfide oxidation experiment. A potential in excess of 4 VDC results in electrolysis of water and decreases the current efficiency for sulfide oxidation. The logical choice for increasing the sulfide destruction rate is to increase the surface area of the electrodes which permits the application of more current through the solution. A current density of 150 Am^{-2} has been reported in the literature for platinized titanium anodes in hypochlorite cells, this current density is probably a good starting point for design of a system (Reference 12). Table 9 lists the sulfate levels during the nearly linear progression of sulfide to sulfate conversion. Levelling off occurs near completion. A graphical representation of the sulfide-to-sulfate conversion is given in Figure 6, which shows sulfate concentration as a function of time. Because of the near neutral pH, some of the sulfide may have been oxidized to elemental sulfur. No analyses were made for total sulfur. However, the most significant result shown in Figure 6 is the reaching of an endpoint for the production of sulfate; we have assumed that this is the endpoint for sulfide oxidation.

Chemical oxidation of the sludges, an alternative to electrooxidation, requires the purchase and storage of chemicals. The amount of

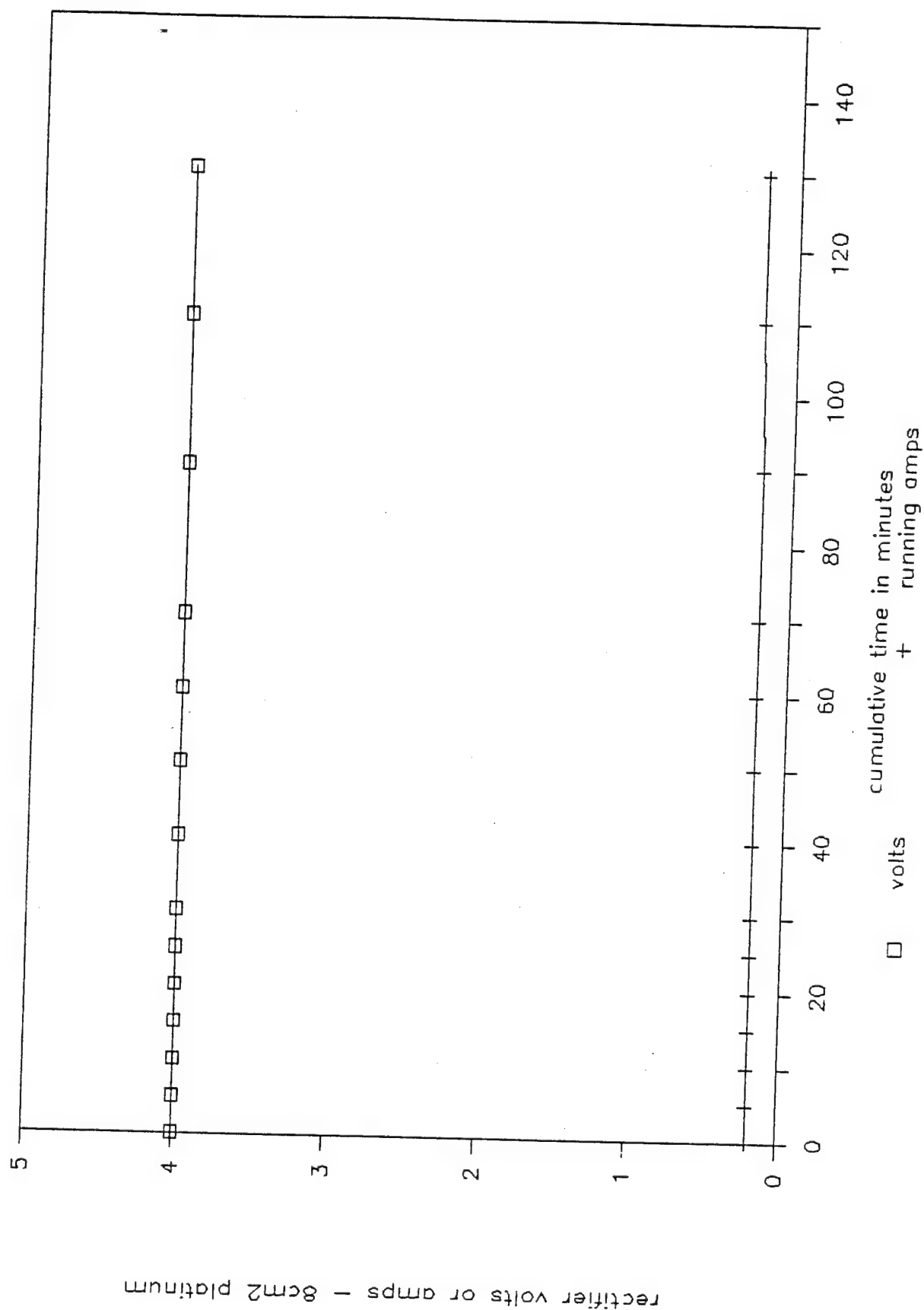


Figure 5. Current vs. Time for Electrooxidation of Sludge.

TABLE 9. SULFIDE TO SULFATE CONVERSION.

<u>Time in minutes</u>	<u>Sulfate in $\mu\text{g/g}$</u>
0	510
5	530
10	560
15	570
20	620
25	680
30	810
40	770
50	930
60	920
70	1100
90	1200
110	1400
130	1400

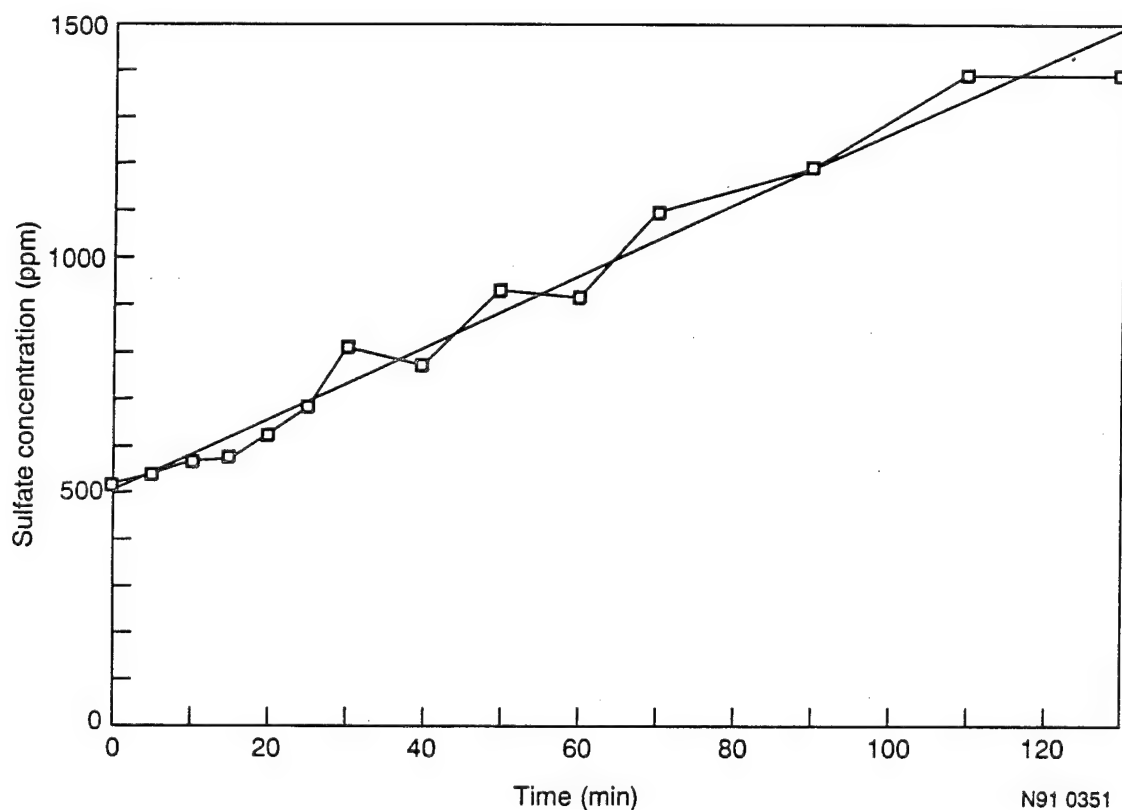


Figure 6. Voltage and Current vs. Time.

chemical used is always in excess of the stoichiometric requirements in order to obtain complete reactions at reasonable conversion rates. In electrooxidation the species required for the sulfide oxidation are produced in situ and are consumed rapidly. The chemical input is sodium chloride (table salt) which is inexpensive and easy to store.

The electrooxidation can be accomplished by a current of 0.016 amps/centimeters² at 4 volts direct current to electrooxidize 1 gram of sulfide sludge solids in one hour (1 percent sludge solids, 1 percent sodium chloride, total volume 200 milliliters, pH 7, electrode surface areas 8 centimeters² each with 1 centimeter spacing). The electrooxidation, as demonstrated by the curve in Figure 6, is seen to be effective at destroying the sulfides.

The oxidation can be performed in either batch or continuous reactors. Continuous flow treatment would require a minimum residence time of 2 hours per unit volume of sludge (based on the same electrode geometries and percents solid as the example above). For such a residence time, the electrooxidation chamber should be capable of holding 42 to 84 gallons of sludge (500 to 1000 gallons/24 hours from the flotation unit). Required anode and cathode surface areas would be approximately 3 to 5 meters² each. Internal mixing of the sludge may be required during electrooxidation to permit good contact between the chlorine in solution and the sulfide solids. Mixing can usually be accomplished by a gentle air sparge from the bottom of the cell; other mechanical mixing should not be necessary.

Engineering design of an electrooxidation system is not well established. The work reported here was done using graphite or platinum electrodes. Platinum electrodes may present security problems in any plant and graphite electrodes may not have sufficient stability over the pH range of interest. Platinum or platinum group metals plated onto an iron or titanium support may provide the necessary surface at lower capital cost and a diminished security risk. Lead oxide on a titanium support has been suggested for chlorine generation (Reference 13), but this coating may not be rugged enough for the present application.

.b. Hydrogen Peroxide Oxidation

Hydrogen peroxide, H_2O_2 , was considered in this study as an alternative for oxidation of the sulfides in the Tinker AFB sludge. It is included as a candidate process for evaluation and to develop data to enable technical and economic comparisons of the processes.

Hydrogen peroxide has been used for many years for treatment of certain waste waters. A primary application of H_2O_2 has been for the destruction by oxidation of H_2S for odor abatement and corrosion control. Also, H_2O_2 has the capability to destroy cyanides and certain organics, but its ability to destroy the greases and oils in the Tinker AFB sludges by oxidation is very limited. In view of these capabilities, and notwithstanding the limitation noted, H_2O_2 is clearly a candidate method as a practical method for destroying the sulfides in the Tinker AFB sludges.

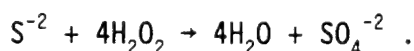
As with any strong oxidizer, certain hazards are inherent when handling and storing H_2O_2 in the concentrated form. Concentrations of 30 to 50 percent are available in drums, and concentrations of 70 percent are available in bulk (tanker trucks and rail cars). While H_2O_2 by itself is neither flammable or explosive, its decomposition generates heat and liberates oxygen. In dilute form the heat is easily absorbed by the water, but in concentrated form the increased temperature will accelerate decomposition and the liberated oxygen and steam may result in container failure. An oxygen-enriched atmosphere may result in combustion of materials not normally considered flammable, and/or unstable reaction products may be generated.

The expected rate of decomposition of properly stored H_2O_2 ranges between 1 and 2 percent per year. Vented storage vessels are mandatory, and vessels and transfer piping must be scrupulously clean and designed so that H_2O_2 solution cannot be trapped between two closed valves or drawn back into the storage vessels. Many impurities catalase H_2O_2 decomposition, a situation that may be beneficial when treating wastes, but hazardous if the impurities enter storage vessels or transfer piping.

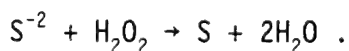
(1) Experimental

A synthetic sludge was generated in order to have a uniform, reproducible material to use for conducting some of the initial experiments, and to avoid the problems associated with shipping and treating hazardous waste from Tinker AFB. The synthetic sludge contained no oil or grease. The method used for generating this sludge was patterned after the procedure given in Reference 1. When dried, the sludge contained 35.1 percent Fe, 11.12 percent S, 9.1 percent Cr (as Cr^{+3}), 3.4 percent Al, and 0.91 percent each of Ag, Cd, Cu, Mn, Ni, Pb, Sn, and Zn (7.26 percent, total).

Based on the formulation of the synthetic sludge, dry 10 gram samples of sludge contained 1.1 grams of sulfur in the form of sulfides of the various contained metals. In order to completely oxidize the sulfides to sulfates, 4 moles of H_2O_2 is required in an alkaline solution ($\text{pH} > 8$) for each mole of S^{-2} , according to the reaction:



In a neutral or acid solution, 1 mole of H_2O_2 will reduce 1 mole of S^{-2} to 1 mole of elemental sulfur, according to the reaction (References 14 and 15):



The stoichiometry of the reactions was used to estimate the amount of 30 percent H_2O_2 required to oxidize the synthetic sulfide sludge. The 30 percent H_2O_2 solution contains 0.334 gram H_2O_2 per milliliter.

Three samples of 10 grams sludge each were placed in 400 milliliter beakers and sufficient deionized water was added to each beaker to produce a total volume of 100 milliliters, which produced slurries containing about 10 percent solids. The pH of the resulting slurries was about 4, so the pH was increased from 4 to 9 in two of the slurries using either NaOH (Treatment A) or NH_4OH (Treatment B), and was decreased to 2 in the third slurry using H_2SO_4 (Treatment C). For this oxidation study, 30 percent H_2O_2 was added without

dilution to the 10 percent slurry using a burette. To completely oxidize the 1.1 grams of sulfide contained in the 10 grams sample, 4.72 grams of H_2O_2 or 14.1 milliliters of 30 percent H_2O_2 would be required. A total volume of 25 milliliters was used for each of the samples to ensure that all of the sulfide was oxidized. Reagent addition was made at a rate of 0.8 to 1.0 milliliter per min (0.27 to 0.33 gram of H_2O_2 per min). A magnetic stirrer was used to maintain the solids in suspension during reagent addition to ensure better H_2O_2 access to the sulfides.

The presence of even trace amounts of Fe, Cu, and other metal ions will catalyze the decomposition of H_2O_2 (but not necessarily the reaction with S^{-2}) and make the decomposition product (O_2) more available for sulfide oxidation. Some foaming was evident on the surface of the solutions soon after the addition of H_2O_2 began, indicating O_2 evolution, and the foaming continued for more than 15 minutes after the 25 milliliter addition was completed. The O_2 that escapes in this manner is unavailable for reaction with S^{-2} , thus the need for excess reagent as noted above.

The slurries were allowed to stand overnight, after which they were filtered and the residue was washed. Samples of each of the filtrates were analyzed to enable an estimate of the effectiveness of this treatment and the analytical data are given in Table 10. The solutions were saved for subsequent treatment with ion exchange resins and sodium borohydride (SBH) to study metal removal and separation approaches.

If the H_2O_2 treatment had been 100 percent effective, all of the sulfides would have been converted to sulfates and solubilized except for Ag, Pb, and Sn. The Ag would remain in the residue as a chloride, PbSO_4 is nearly insoluble, and the Sn would likely remain behind as SnO_2 . The relative immobility of these elements is confirmed by the analytical results given in Table 10. Based on the sulfur analysis, only 15 to 20 percent of the total contained sulfur was oxidized by the H_2O_2 . It would appear that Treatment C had no effect on the sulphur content of the sledge; however, the analytical technique

TABLE 10. AQUEOUS PHASE COMPOSITION AFTER H₂O₂ TREATMENT OF SLUDGE.

Soln (pH)	Fe	Cr	Al	Ag	Cd	Cu	Mn	Ni	Pb	Sn	Zn	S
A (9)	26	0.2	45	ND	181	85	66	127	2.6	ND	137	228
B (9)	53	0.5	96	ND	286	140	94	186	3.6	ND	221	357
C (3)	174	0.4	202	ND	242	94	91	158	5.3	ND	219	335
Results in parts per million							ND = Not Determined					

was unable to distinguish between sulfides, sulfates, and elemental sulfur. Based on the results in Table 10, no particular advantage was evident, raising the pH with NaOH compared to NH₄OH (Treatment A vs. B). Generally, oxidation at higher pH was slightly more effective than low pH (Treatment C). Possible additional experiments should be considered using higher pH, slower rates of H₂O₂ addition and/or dilution of 30 percent H₂O₂ to 3 percent or less, higher temperatures, and pressurizing the reaction vessel. In lieu of pressurizing the vessel, a deep bath could achieve the same effect if the H₂O₂ were admitted near the bottom of the vessel.

c. Wet-Air Oxidation Treatment

The Wet-Air Oxidation (WAO) process is based on the discovery that many compounds will oxidize readily in an aqueous phase at temperatures less than the critical temperature of water. The process is an accepted approach to treatment of certain wastes (References 16-18). Zimpro-Passavant, Rothschild, WI, has extensive experience in WAO and was contracted to treat samples of Tinker AFB sulfide sludge with the WAO process to determine its applicability. The Zimpro process is claimed to become self-sustaining in the chemical oxygen demand (COD) range of about 15,000 milligrams per liter or greater. The sulfide sludge had a COD of 15,432 milligrams per liter. The products had a COD about half of that of the feed. Addition of a hydrocarbon to the sludge would probably not be beneficial.

Wet-air oxidation of the Tinker AFB sulfide sludge involves high temperature/high pressure treatment of the aqueous sludge suspension. These conditions greatly accelerate oxidation reactions of sulfides and the

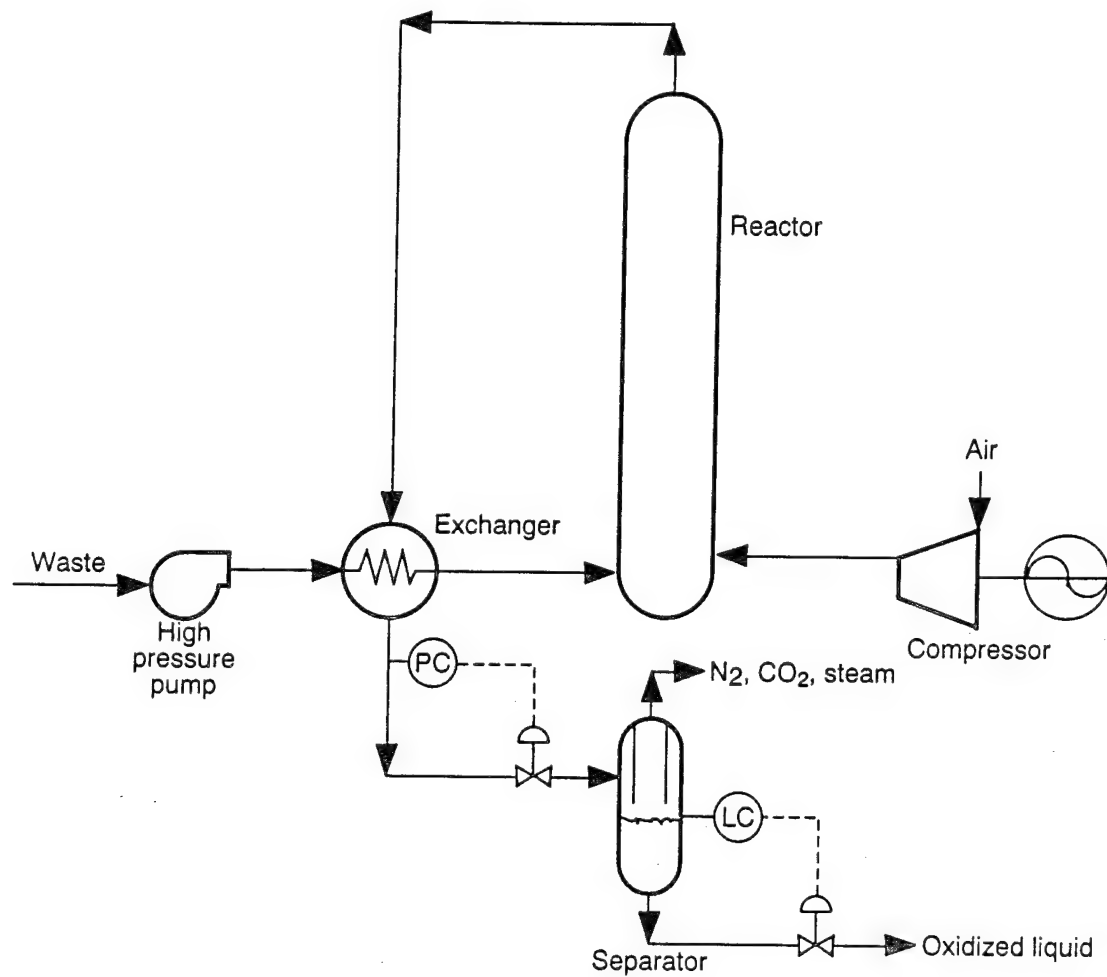
hydrocarbons. Once initiated, the reactions may generate sufficient heat to be self-sustaining and not require additional fuel, provided that the feed is sufficiently rich. Oxygen is supplied by compressed air, although pure oxygen may be used.

The WAO tests performed by Zimpro/Passivant were carried out in 500 milliliter autoclaves. The autoclaves were charged with waste and sufficient compressed air to yield an excess of residual oxygen following reaction. The charged autoclaves were placed in a heater/shaker mechanism and then heated to the 200, 240, or 280°C test temperature for 1 hour. At the end of the test period, the autoclaves were cooled to room temperature and depressurized. These treatments reduced the chemical oxygen demand (COD) of the slurries by 48.8, 70.8, and 79.3 percent at 200, 240, and 280°C, respectively. The remaining COD after the 280°C treatment usually consists of acetic and/or formic acid, the intermediate oxidation products from partial oxidation of the oils in the feed. The oxidized effluent appeared "slightly gold" in color and suspended solids, which appeared to be metal oxides, settled out rapidly. Analysis of the effluent from the 200°C treatment indicated that the total sulfur measured was in the form of sulfate. The pH of the solution dropped from about pH = 9 to a range of pH = 3.5 - 3.8 upon oxidation. Chemical analysis of the solution are given in Table 11. No other chemical analyses were performed to determine the composition of the solid residue or the heavy metals in solution.

Screening tests were performed to provide data for construction materials for the system. These tests were carried out in shaking autoclaves similar to those used for the wet-air oxidation tests. The tests were run at 250°C for 300 hours at pH 7.2 to 3.6. The corrosion coupons were welded U-bends fabricated from commercial sheet stock of various alloys. The coupons were not annealed after welding, resulting in a plastically-strained, residually-stressed metallurgical state. Teflon washers were used to electrically insulate the coupons and provide a crevice area for monitoring of crevice corrosion. Pretest and posttest coupon cleaning was with 10 percent nitric acid. Weight loss was measured to determine the general corrosion weight of each coupon. Visual and microscopic examinations were performed to identify the presence of any localized corrosion. A schematic of the system is shown in Figure 7.

TABLE 11. TEST CONDITIONS AND RESULTS FOR WET-AIR OXIDATION OF SLUDGE.

		<u>As Received</u>		<u>Oxidized Products</u>	
Oxidation Temperature, °C	-	200	240	280	
Time at Temperature, min.	-	60	60	60	
mCOD	mg/L	15432	7900	4500	3200
COD Reduction	%	-	48.8	70.8	79.3
T BOD	-	2179	2764	2017	2346
T BOD/COD Ratio	0.141	0.35	0.45	0.73	
PH	7.12	3.8	3.7	3.6	
NPOC	mg/L	4.9	1988	2094	1661
POC	mg/L	11.0	272	286	441
Sol. Chloride	mg/L	< 5.0	57.0	43.8	69.5
Total Solids	mg/L	5880	5000	3010	3300
Total Ash	mg/L	2050	2700	2300	2700
Suspended Solids	mg/L	5360	600	1304	1360
Suspended Ash	mg/L	1740	510	1176	1260
Total Sulfur	mg/L	190	187	187	219
Sulfide-S	mg/L	128	<1.0	<1.0	<1.0
Sulfate-S	mg/L	<54.9	317	165	190



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Figure 7. Basic Wet Air Oxidation Flow Scheme.

The materials tested for corrosion resistance are shown in Table 3 with their general corrosion rates. Type 316L stainless steel (SS) and Alloy 20 had good general corrosion rates but showed pitting. The 316L SS exhibited transgranular stress corrosion cracking (TGSCC). The low pH of the oxidized sludge and the presence of chlorides could account for the pitting and the TGSCC. The results show that alloys 625, C-276, and titanium Grade 2 would all be acceptable materials. The general corrosion rates were less than 0.002 inches per year and none of these alloys showed TGSCC. Alloy 625 would be the most economical of the acceptable materials of construction; however, pH control to higher levels could result in a less expensive material.

3. Liquid-Phase Processing

Liquid-phase processing is performed after the SCC sludge solids have been subjected to the oxidation step. If the sulfides have been totally oxidized to sulfate, and the iron, chromium, and aluminum have been converted to oxides and/or hydroxides, it should be convenient to effect a separation of the soluble sulfates from the insoluble oxides/hydroxides in the pH range of 3 to 9. Below pH = 3, ferric hydroxide becomes soluble; above pH = 9 aluminum hydroxide starts to solubilize. Most of this separation can be accomplished by settling. The liquid phase will contain the soluble sulfates of the heavy metals. This section describes treatments applied to the liquid phase to remove these metals. These treatments are: sodium borohydride (SBH) reduction, ion exchange separation, and electroplating reduction.

a. Sodium Borohydride Reduction

Sodium borohydride (NaBH_4 or "SBH") is a mild reducing agent that is able to reduce some of the metal sulfates in solution to elemental metals that will settle as a dense, compact precipitate. SBH is a white crystalline solid. Morton Thiokol markets VenMet™, a solution of 12 percent SBH and 40 percent NaOH in water. The solution is stable (less than 1 percent decomposition per year) and is handled in commerce as a 50 percent caustic solution.

The easily reduced metals such as Ag, Cd, Cu, Ni, and Pb are amenable to SBH treatment. The process is becoming well-established in industry, especially for recovery of precious metals from aqueous effluents where residual metals can be reduced to below parts per million levels. Ideally, one equivalent of SBH will reduce 8 equivalents of metal, according to the reaction:



In practice, some H_2 is evolved if hydrolysis of SBH occurs when the pH is too low and/or the temperature is too high. Generation of H_2 is minimized by pH and temperature control, as well as by diluting the SBH solution (10:1) and adding it slowly. While the quantity of hydrogen generated is usually very small, it is good practice to provide adequate ventilation in the vicinity of the operation.

Industrial treatment of solutions carrying heavy metals is usually a batch process. A sample of the batch was withdrawn and tested to enable a fairly precise estimate of the amount of reagent required and the metal expected to be recovered when the batch is treated. A preliminary step in testing the sample is to determine the quantity of sodium bisulfite (NaHSO_3 or SBS) needed to react with oxidants that may be present. This reagent will react with any remaining H_2O_2 present and will also prevent precipitated metals from reentering solution. The addition of SBS reduces unnecessary SBH consumption. SBS is much less expensive than SBH.

If the SBH treatment is applied to the solution resulting from treating 10 grams of a synthetic sludge sample with H_2O_2 , 0.142 grams of each of the metals should be in the solution that is separated from the hydroxides, assuming 100 percent recovery efficiency. Exceptions will be PbSO_4 , AgCl , and SnO_2 , which should remain with the hydroxides due to their relative insolubilities. Assuming no Cr, Fe, and Al carryover, Cd, Cu, Mn, Ni, and Zn ions will be in the solution to be treated.

The SBH solution was prepared with 12 percent NaBH_4 and 40 percent NaOH, and deionized water was added so that the solution was

equivalent to VenMet™ when diluted 10:1. Stirring bars were placed in 400 milliliter beakers and 150 milliliters of solution resulting from H_2O_2 oxidation of the sulfides was placed into each beaker. About 3 milliliters of 5 percent SBS solution was added to each beaker, the pH was adjusted to 5 to 6 using NaOH, and the SBH solution was added dropwise from a burette. The solution became black quickly from very small particles of reduced metal and it was difficult to determine visually when the endpoint was reached. An oxidation-reduction potential instrument would have been useful for this determination. The precipitate was allowed to settle and an additional drop of SBH was added; the clear portion of the solution was observed carefully to determine if any additional reduction occurred in the vicinity of the added drop. If not, metal removal was considered to be complete. Only one of the three solution samples required additional SBH; apparently the endpoint had already been reached in the others when this test was applied.

The results of the SBH treatment were determined by analyzing the solutions after separating them from the precipitate by decanting and filtering. The analytical results are given in Table 12. Solution designations A, B, and C correspond to the treatments given prior to the H_2O_2 additions as described earlier under Hydrogen Peroxide Processing.

The results in Table 12 compare the solution concentrations after the SBH treatment with the original solution composition. Not shown in the above analytical results is 44 parts per million Fe in the "C" solution. Generally, the SBH treatment was most effective on the "A" solution, with only Cd remaining above tolerable levels. With the other solutions, some of the metals may have redissolved because of residual ammonia or low pH when the solutions were allowed to stand to enable the solids to settle. Some additional work is needed to refine this technique.

b. Ion Exchange Separation

Ion exchange is a well-established process for separating and concentrating metal and nonmetal ions from solution. Water softening is a common

TABLE 12. ANALYSIS OF SOLUTION AFTER SBH TREATMENT.

Soln	Ag	Cd	Cu	Mn	Ni	Pb	Sn	Zn
A	ND	56 (181)	0.9 (85)	43 (66)	0 (127)	ND (2.6)	ND	0.1 (137)
B	ND	258 (286)	4.0 (140)	86 (94)	149 (186)	0.3 (3.6)	ND	170 (221)
C	ND	199 (242)	0.9 (94)	78 (91)	86 (158)	0.1 (5.3)	ND	68 (219)
Results in parts per million ($\mu\text{g/mL}$)						ND = Not Detected		

use of ion exchange technology; recovery of uranium from leach solutions is another. The tests reported here were undertaken to determine if ion exchange would be viable for treatment of the solutions resulting from oxidation of the sulfide sludge.

The following technical information for four candidate cation exchange resins is provided by the manufacturers.

Type	Functionality	meq/mL	CEC* Range	pH	Bulk Density
DP-1	Methacrylic	Carboxilic	2.5	5-14	0.74 g/mL
IR-120+	Styrene/DVB**	Sulfonic Acid	1.9	0-14	0.77-0.87 g/mL
IRC-718	Styrene/DVB	Iminodiacetic Acid	1.1	2-14	0.67 g/mL
CSA MS5	Styrene/DVB	Iminodiacetic Acid	1.1	1-14	0.72 g/mL

*CEC = Cation exchange capacity

**DVB = Divinyl benzene, used to crosslink the styrene

(1) Cation Exchange Capacity Determination

"Calibration" of these resins was necessary to determine their total cation exchange capacity (CEC) prior to conducting the experimental work. The resin calibration was done using ASTM procedure D2187-74, Methods A, B, E, and F. This procedure is described in Appendix A.

For each resin test, a solution was formulated which that expected if oxidation of the sulfides in the sludge was 100 percent effective. Sufficient resin was added to each solution to totally remove the metal ions of interest, with capacity to spare, based on the manufacturers' CEC as given above. The solution pH was then adjusted to 4, 7, and 9 for each test and the resins and solutions were stirred together overnight. The resins and any residues were separated from the solutions by filtering, and the solutions were analyzed to compare the effectiveness of the resins. The data resulting from the calibration study were used as the basis for selecting a resin and determining the quantity needed to strip the metal ions from the solutions. As a result of the calibration study, the CSA MS5 resin appeared to have the highest capacity for the ions of interest and was chosen for further testing in solutions resulting from actual sulfide sludge oxidation tests. The IRC-718 resin gave nearly the same results as the CSA MS5 and could be considered as equivalent.

The solutions resulting from the H_2O_2 treatment of the sludge were circulated through a small glass column containing a 1.0 gram sample of CSA MS5 resin. Glass wool plugs were inserted in each end of the column and sufficient free volume was included between the plugs to allow for resin expansion resulting from water absorption and ion accumulation. A peristaltic pump was used to circulate the solution from the beaker to the column and back to the beaker at 85 milliliters/minute. This was a recirculating rather than a "once-through" system that would be anticipated for the pilot plant.

The pH of the sample solutions had dropped from 9 prior to the H_2O_2 treatment to about 4 due to formation of sulfate ion and hydrolysis to produce sulfuric acid. No attempt was made to increase the pH prior to circulating the solutions through the resin columns since the results obtained during resin testing were generally good at low pH, although more resin was needed at low pH since the "per gram" resin capacity decreased due to competition from H^+ ion.

The CSA MS5 resin performed better in the calibration test where no iron was present than in the solutions derived from sludge oxidation, although the selectivity for iron is low. Cd, Mn, and Zn remained at

fairly high levels (75 to 125 parts per million, 45 to 56 percent removal) in the solutions after resin treatment, while Ag, Cu, Pb, and Sn were present at concentrations less than 1 parts per million. The Ag, Pb, and Sn were low in the solutions resulting from the oxidation step due to the formation of nearly insoluble compounds that remained behind with the filter residues. While raising the pH to 9 with NH_4OH produced more ions in solution after H_2O_2 treatment than did raising the pH with NaOH, resin recoveries were somewhat higher when the NaOH was employed. This may have been a result of competition from the NH_4^+ ion, although not much NH_4^+ was expected to be present at the pH used for the ion exchange test. To facilitate comparison, Table 13 was organized in the same manner as Table 12, with the composition of the original solution in parentheses.

Comparing the analytical results in Table 12 and Table 13 it appears that the resins were less effective in stripping the heavy metal ions from solution than was SBH. It is possible that a resin specific for Cd could be employed after SBH treatment, but this was not investigated. In view of the above results and considering the vulnerability of resins to organic contaminants, it did not appear that the investigation of resins should be pursued. Consequently, resin regeneration tests to determine effectiveness of procedures for eluting metals from the resins were not performed, nor were the resins exposed to solutions produced by oxidation of Tinker AFB sulfide sludge.

c. Metal Electrodeposition During Electrooxidation

Electrodeposition of metals occurred as a consequence of electrochemical reduction. Although electrowinning is attractive in terms of low chemical input, the metal concentrations appear to be too low to make efficient use of this technique. Table 14 shows the percent of five major sludge metals that were removed during the course of a 1 hour plating treatment of Tinker sulfide sludge using 4.0 VDC at 1 ampere for 100 milliliters of sludge of 5 percent solids at pH 7 and 1 percent sodium chloride.

During the experiment, approximately 5 percent of the total available metals were plated. The first hour of electroplating from the sludges delivered from the SCC via froth flotation would consume approximately

TABLE 13. ANALYSIS OF SOLUTION AFTER ION EXCHANGE SEPARATION.

Soln	Ag	Cd	Cu	Mn	Ni	Pb	Sn	Zn
A	ND	98 (181)	0.8 (85)	79 (66)	16 (127)	0.1 (2.6)	ND	76 (137)
B	ND	125 (286)	2.9 (140)	82 (94)	38 (186)	0.5 (3.6)	ND	99 (221)
C	ND	186 (242)	1.2 (94)	92 (91)	51 (158)	1.2 (5.3)	ND	163 (219)
Results in parts per million ($\mu\text{g}/\text{milliliter}$)							ND = Not Detected	

TABLE 14. METAL REMOVAL BY ELECTROWINNING.

	μg of metal available	μg of metal plated	percent of metal plated
Cr	2900	98	3.4 percent
Fe	2300	185	8.0%
Al	600	28	4.7%
Ba	220	39	18%
Ni	200	26	13%

145 kilowatt-hours of power and return only 14 grams of metal. The presence of barium and aluminum in the deposited metal is attributed to occlusion of these metal ions in the plated metals.

4. Solids Processing

For many years ferroalloys have been produced commercially by the carbothermic reduction of oxide ores and by remelting of ferroalloy fines. Ferroalloys are used primarily as master alloys to enable addition of specific elements to steel to improve the physical and chemical properties. Chromium, manganese and silicon are the major ferroalloys added to steels. A byproduct of ferroalloy production is the slag phase. In the present project, this slag phase is a ceramic waste form that contains the bulk of the nonferroalloy materials present in oxidized sludge solids.

a. Ferroalloy production

Producing ferroalloys of chromium, manganese, and silicon is easier and cheaper than producing these metals in unalloyed form. In general, the presence of iron in the reaction system improves the operating conditions, as well as the yield of the alloying element. The melting point of the iron

alloy and the iron-carbon eutectic are both lower than that of chromium, manganese, and silicon metal. The collection of the product as a ferroalloy, therefore, allows operation at lower temperatures, and the lower temperatures decrease heat losses and are less aggressive to refractories. In an iron-based system, carbon (in the form of metal carbide) dissolved in the oxide slag and iron melt may be a more effective reducing agent than solid carbon. The oxide can be reduced by dissolved carbon with subsequent removal of the metal from the reaction system by solution in the iron melt.

Carbothermic reduction involves the reaction of metal oxide with carbon to produce carbon monoxide gas, intermediate oxides, metal carbides, and metal. In practice, an excess of chromium oxide is usually present in the slag, and high-carbon, molten iron forms first and acts as a solvent for chromium carbides to produce ferroalloys. The basic reactions are:



The minimum temperature for operation of the reaction can be determined from the free energy of formation, which is a measure of the tendency for a reaction to occur. Free energy is a function of temperature, and reactions are favored above the temperature at which $\Delta G = 0$. From the value of ΔG , the equilibrium conditions can be calculated ($\Delta G = 0$) for the activity or concentration of the reactants and products. For most oxide/carbide/metal systems, the free energy at a given temperature is the least for carbide formation, Reaction (1), i.e., the favored product of carbothermic reduction of an oxide is not the metal, but the metal carbide. Formation of the metal depends on the intermediate oxide/carbide reaction, Reaction (3). This reaction generally has the highest free energy of formation (ΔG is more positive than for the formation of carbide) and requires a higher temperature than for direct metal formation, Reaction (2). It is therefore necessary to consider all the existing

oxide/carbide systems to determine the minimum temperature for metal production. Table 15 lists the threshold (equilibrium) temperatures, $\Delta G = 0$, for Reactions (1), (2), and (3) for ferroalloy systems of chromium, silicon, and aluminum. Threshold temperatures are also given for the carbothermic reduction of iron as a comparison.

Reaction temperature—The temperature in the reaction zone should exceed the threshold or minimum temperature as defined by where $\Delta G = 0$ in order for the desired reaction to proceed. Factors limiting the production rate are related to heat and mass transport phenomena between the reactants rather than thermodynamic or chemical kinetic limitations of the reaction.

Carbothermic reactions are best carried out when a liquid phase is present, especially if the carbon is to be introduced as bulk solid and not as the product of gaseous or liquid decomposition (i.e., gas or liquid hydrocarbons). Therefore, for carbothermic reduction to occur, a further criterion is that the reaction zone temperature must exceed the minimum, i.e., it must be higher than where $\Delta G=0$, but also the temperature should be higher than the melting point, T_m , of the highest melting metal in the system. For ferroalloy production, the minimum melting point of the metal may be determined by the temperature at which it dissolves in the available Fe-C melt. The melting temperatures of the metal oxides indicate that these oxides will remain as solids unless a suitable flux (SiO_2 , CaO, borax) is added to enable formation of a slag to facilitate the reduction reactions. The melting temperature of the iron eutectic is less than the melting points of the alloying metal. In general, the minimum reaction zone temperature is dictated by the minimum, $\Delta G=0$ temperature as shown in Table 16.

Energy requirements - heat of reaction, melting, and vaporization—The net energy requirements for the reduction reaction include: (1) the sensible energy for heating the reactants to the reaction temperature, (2) the energy to cause any changes in state (e.g., solid to liquid, liquid to gas), plus (3) the heat for the reaction itself. The gross energy requirement must include additional energy for heating the flux additives and to compensate

TABLE 15. -THRESHOLD REACTION TEMPERATURES, $\Delta G = 0$ IN FERROALLOY PRODUCTION BY CARBOTHERMIC REDUCTION IN OXIDE/CARBIDE/METAL SYSTEMS.

Reaction No. Final Product	(1) Carbide	(2) Metal	(3) Metal
System	Temperature, (°C)		
$\text{Fe}_2\text{O}_3/\text{Fe}_3\text{C}/\text{Fe}$	644	640	571
$\text{Cr}_2\text{O}_3/\text{Cr}_{23}/\text{Cr}$	1,276	1,255	1,734
$\text{SiO}_2/\text{SiC}/\text{Si}$	1,464	1,551	1,733
$\text{Al}_2\text{O}_3/\text{Al}_4\text{C}_3/\text{Al}$	1,923	2,036	2,274

TABLE 16. MINIMUM REACTION ZONE OPERATING TEMPERATURES, T_{RZ} (°C).

System	$T_{\Delta G=0}$	$T_{\text{metal}}^{\text{M}}$	Oxide	$T_{\text{oxide}}^{\text{M}}$	$T_{\text{Fe/X}}^{\text{M}}$	X	%X	T_{RZ}
Fe	644	1,536	Fe_3O_4	1,597	1,147	C	4.3	1,536
Cr	1,734	1,898	Cr_2O_3	2,266	1,510	Cr	20	1,898
Si	1,733	1,413	SiO_2	1,723	1,200	Si	20	1,733
Al	2,271	659	Al_2O_3	2,050	1,232	Al	42	2,271

for losses to the environment. The heat of reaction required for reduction of iron oxide and the alloying metal oxide is a substantial fraction of the net energy required in the system.

The presence of a liquid can be advantageous as a reaction facilitator for reduction of oxides by dissolved carbon in the melt and for solution of the metal product. Reduction of oxides by carbon is highly endothermic and will tend to cool the melt, possibly to the point of solidification. Also, solid carbides may form and coat unreacted oxide particle thereby inhibiting further reaction. It is necessary to operate with a superheated melt to avoid such difficulties.

The ratio of the heat of vaporization to the heat of reaction, and the metal vapor pressure at the reaction zone temperature are given in Table 3. Fortunately, none of metals produced in the production of ferrochromium have appreciable vapor pressures at the reaction zone temperatures, so heat losses from vaporization of metals should be low.

Synthesis of ferrochrome—Most chromium ores consist of spinels of the type $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, similar to the forms of iron and chromium found in oxidized SCC underflow sulfide sludge. The spinel and carbon are mixed with silica to form a slag phase ($T_M = 1,600$ to $1,700^\circ\text{C}$) and iron and chromium are reduced to form ferrochromium in the metallic phase. Iron oxides (FeO) and chromium oxides (Cr_2O_3) dissolved in the slag are reduced by carbon to produce iron metal and chromium carbides. As the reaction temperature is increased, chromium carbides of successively lower carbon are formed, $\text{Cr}_3\text{C}_2 : \text{Cr}_7\text{C}_3 : \text{Cr}_{23}\text{C}_6$, until at about $1,750^\circ\text{C}$, metallic chromium is formed as noted in Table 15. The production of low carbon chromium alloys is, therefore, favored by higher temperature operations.

Finely divided materials or composite pellets of carbon and solid fines react more easily at lower temperatures and produce high-carbon alloys. Slags with high fluidities (high $\text{MgO}/\text{Al}_2\text{O}_3$ ratios) promote the rapid dissolution of ore in the slag and, therefore, higher reaction rates, lower reaction temperatures, and high-carbon alloys.

(1) Experimental

A 30 kilowatt, 4.2 kilocycles per second inductions melter was used to smelt a mixture of iron oxide (FeO or Fe_2O_3) and chromium oxide (Cr_2O_3) that approximated the iron and chromium composition of oxidized sulfide sludge. The metal oxides were mixed with solid carbon (graphite), silica, alumina, and magnesia and placed in a 500 centimeters³ graphite crucible (similar crucibles and refractories are available for production-sized equipment). The loaded crucible was placed inside a nine-turn induction coil. A graphite cover was placed over the crucible and a Type C thermocouple in an alumina sheath (0.5 millimeter O.D.) was installed in the center of the crucible with the tip 1 to 2 centimeters from the bottom of the crucible. The induction coil and crucible were enclosed in an air-tight chamber which was purged with argon during test runs.

(2) Results and Discussion

All smelting tests were performed using mixtures of reagent grade materials. A simulated sulfide sludge was synthesized that approximated the chemical makeup of actual SCC underflow sulfide sludge collected at Tinker AFB. This simulated sludge was then oxidized with hydrogen peroxide to turn insoluble sulfides to soluble sulfates which could be then washed out of the sludge material. This low-sulfur material was then analyzed to determine the forms of iron and chromium present and their relative concentrations so that an appropriate test matrix could be made up for smelting tests.

A series of six experiments was performed to test how well the chromium and iron found in the oxidized form of the sulfide sludge could be reduced to form ferrochromium alloy and how much chromium would be left in the slag matrix. No sulfur or sulfates were added to the test mixture because it was determined from the literature that any sulfur present would be volatilized from the slag between 600 and 800°C.

(3) Conclusions and Recommendations from Ferroalloy Formation

Smelting of SCC underflow sulfide sludge is a viable process to recover iron and chromium values from the sludge. Energy costs for a reasonably efficient smelting process should be about 1500 kilowatts per metric ton of sludge (\$75/ton for \$0.05/kilowatt-hour electricity). Organic content in the sludge would cause a corresponding increase in off-gas load for treatment system. No other problems are foreseen due to organic content in the sludge.

The recommendation is made that the feed stock should be pelletized to decrease reaction and dissolution times. The process should be made continuous to improve economics. One additional recommendation is that the sulfur content of the sludge be kept below 1 percent for thermal treatment of the sludge. Sulfides and sulfates result in acidic and corrosive off-gases that could severely damage off-gases treatment systems.

b. Ceramic Wasteform Generation

Vitrification of hazardous waste streams containing heavy metals a viable method for stabilizing inorganic materials and for destroying organics that may also be in the waste stream. Wastes containing metals are melted, along with some silicate material (usually soil). The metals are oxidized and form compounds with the silicates present. All metal oxides in the original waste are tightly bound in the matrix of the resulting vitreous slag and are highly resistant to leaching. At the temperatures necessary to melt the waste and form the slag, any organic materials present are pyrolyzed to form carbon dioxide and water which pass through the off-gas handling system.

The present process involves mixing the waste stream with 40 to 60 percent clean soil or a mixture of silica (SiO_2), alumina (Al_2O_3), and magnesia (MgO) and heating this mixture to its melting point (1,200 to 1,600°C) in an oxygen atmosphere. The metals are oxidized and form a solid solution with the silica/alumina/magnesia matrix (slag). Under these conditions, the organics present are pyrolyzed to form carbon dioxide and water and are carried off in the

off-gas stream. The metals are very tightly bound in the slag matrix and pass the toxicity characterization leaching procedure (TCLP) described in Appendix A of the Environmental Protection Agency Regulations (Reference 19) for identifying hazardous waste tests even when the slag is finely ground (<100 mesh).

(1) Experimental

A 30 kilowatt, 4.2 kilocycles per second induction melter was used to melt a mixture of iron oxide (FeO or Fe_2O_3) and chromium oxide (Cr_2O_3) that approximated the iron and chromium composition of oxidized sulfide sludge. The metal oxides were mixed with silica (SiO_2) and alumina (Al_2O_3), and placed in a 500 centimeters³ calcia stabilized zirconia surrounded by a 1 centimeter thick graphite sleeve, which in turn was placed inside a nine turn induction coil. A graphite cover was placed over the crucible and a Type C thermocouple in an alumina sheath (0.5 millimeter O.D.) was installed in the center of the crucible with the tip 1 to 2 centimeters from the bottom of the crucible. The induction coil and crucible were enclosed in an air-tight chamber which was purged with argon during test runs.

(2) Results and Discussion

All vitrification tests were performed using mixtures of reagent grade materials. A simulated sulfide sludge was synthesized that approximated the chemical makeup of actual sulfide sludge collected at Tinker AFB. This simulated sludge was then oxidized with hydrogen peroxide to turn insoluble sulfides to soluble sulfates which could be washed out of the sludge material. This low sulfur material was then analyzed to determine the forms of iron and chromium present and their relative concentrations so that an appropriate test matrix could be made up for melting tests. The iron/chromium ratio was determined to be 3.85 in the oxidized sludge. After the first test was performed it was determined that some alumina was necessary to lower the viscosity of the slag. On all subsequent tests alumina was added as 1.5 percent of the silica used.

A series of five experiments was performed to test how well the chromium and iron oxides would be bound to the slag matrix. No sulfur or sulfates were added to the test mixture because it was determined from the literature that any sulfur present would be volatilized between 600 and 800°C. Experimental conditions for these tests are summarized in Table 17.

An additional set of tests was planned to determine the required hold time at the melting temperature to ensure complete dissolution of oxidized metals into the slag. In the first series of tests it was observed that complete dissolution occurred within minutes of reaching the melting temperature of the slag.

X-ray diffraction (XRD) analysis was used to identify crystalline phases present in the slag in concentrations greater than 1 wt percent. The presence of silica, chromium oxide, and maghemite (a metastable form of hematite, Fe_2O_3) are indicators of incomplete melting. When the mixture of iron oxide, chromium oxide, and silica are completely melted ($>1710^\circ\text{C}$) the resulting solid solution should contain cristobalite (SiO_2), fayalite (Fe_2SiO_4), chromite (FeCr_2O_3), and silicates of iron and chromium.

In addition to XRD determination of the major crystalline phases present in the slag, chemical analysis was performed on the slag to determine total metals content of the slag. Sodium borate was mixed with ≈ 0.0500 grams of finely ground slag and the mixture heated to melting to dissolve the silicate material. The resulting fused material was then dissolved in nitric acid and diluted to 25 milliliters for chemical analysis using an inductively coupled plasma (ICP) spectrometer.

Tests were conducted to determine the leachability of iron and chromium from the slag under acidic aqueous conditions. These tests were conducted using a modified TCLP test procedure, i.e., 5.0 grams of material for the leach test instead of the prescribed minimum of 100 grams of material. Less than 100 grams of slag were produced during each test necessitating the use of smaller samples.

TABLE 17. FERROCHROMIUM SMELTING TESTS AND AMOUNTS OF MATERIAL USED FOR EACH TEST.

Sample =>	FECR-1	FECR-2	FECR-3	FECR-4	FECR-5	FECR-6
Smpl wt. (g)	446.15	607.3	344.1	365.3	384.8	200g
Cr ₂ O ₃	21.15	42.3	63.4	21.1	42.3	oxidized
FeO or Fe ₃ O ₄	200.00	300.0	150.0	113.0	150.0	TAFB Sludge
Carbon	75.00	75.0	75.0	95.0	66.8	88.2g
SiO ₂	100.00	150.0	150.0	75.0	85.0	150.0g
Al ₂ O ₃	25.00	20.0	20.0	20.0	20.0	20.0g
MgO	25.00	20.0	20.0	20.0	20.0	20.0g
Power in	16.0 kW	16kW	7.2	7.0	7.0	7.0
Heat Rate (°C/sec)	0.80	0.75	0.30	0.28	0.31	0.24
Highest t (°C)	1,851	1,810	1,780	1,375	1,852	1,675
Time @ HT	20 min	15.0	10.0 min	0.0 min	5.0 min	15.0 min

TABLE 18. CHROMIUM AND IRON LEACHED FROM SLAG IN ACIDIC SOLUTION VIA TCLP.

Slag Sample I.D.	Sample wt. (g)	Extractant Volume (ml)	Fe Extracted (mg/L)	Cr Extracted (mg/L)
FC-1A	5.0227	100	315.1	1.240
FC-1B	5.0227	100	315.8	1.440
FC-2	5.0255	100	392.1	0.950
FC-3	5.0250	100	328.9	1.390
FC-4	5.0115	100	449.8	0.400
FC-5	5.0629	100	14.5	<0.002
FC-6	5.0352	100	47.8	0.100
EPA Limits	-----	---	NA	5.00

The results of the leaching tests are shown in Table 18. While the acidic extractant was able to mobilize some iron, chromium present was very resistant to leaching and the solution contained less than the allowable chromium set by current EPA standards in the extractant solution. Since iron oxide should readily form complexes with silica, a longer hold time at the slag melting point or higher temperature may be required if lower leach rates for iron are desirable. Lower leach rates for iron may be required to meet EPA drinking water standards, although the EPA currently has no limits on iron for TCLP tests. A more oxidizing atmosphere over the melt coupled with a longer hold time would ensure complete oxidation of remaining free iron and enable formation of the less leachable silicate compounds.

(3) Conclusions and Recommendations from Ceramic Wasteform Generation

Thermal treatment of Tinker AFB sludge to produce a vitrified product will result in an environmentally safe glassy slag that will pass EPA TCLP tests. Energy costs for a reasonably efficient thermal treatment system where sludge is mixed with soil in a 60:40 soil:sludge ratio should be less than 500 kilowatt per metric ton (\$25/ton for \$0.05/kilowatt-hour electricity). Loading rates up to 45 wt percent iron and chromium oxide can be achieved. Ceramic waste form synthesis economics could be improved by development of a continuous process. Organic content in the sludge would cause a corresponding increase in the load on off-gas treatment systems. No other problems are foreseen due to organic content in the sludge.

The recommendation is made that the feed stock be pelletized to decrease dissolution time. A further recommendation is made to add a low melting soil or add magnesia and calcia to lower the melting point of the slag. An additional recommendation is that the sulfur content of the sludge be kept below 1 percent for thermal treatment of the sludge. Sulfides and sulfates result in acidic and corrosive off-gas that will severely damage off-gas treatment systems.

D. TASK 4: PROCESS ECONOMIC EVALUATION

Based on the information generated during bench-scale testing, an economic analysis was prepared to provide an overall estimate of the cost of a full-scale facility for treating the SCC sludge and a preliminary determination of the products and/or waste streams of the processes. The economic analysis was not intended to include a detailed cost estimate, but would give a rough order-of-magnitude cost that would aid in the construction of a pilot-plant facility.

This economic analysis supplies cost estimates for a full-scale facility and will rely on stream qualities predicted from laboratory tests and vendor information. The utility requirements and cost of auxiliary systems will also be based on testing data or vendor information. This economic evaluation presents quantitative values and will not select from among the individual processes available for the treatment process. Based on the information presented in this evaluation and the opinion of the evaluating engineer, recommendations for the processes to be demonstrated will be presented in section IV of this report, Task 5, Conceptual Pilot Plant Design.

1. Process Flowsheet and Description

The processes selected to recover metals from the IWTP metal-sulfide sludge are outlined in Figure 8. The individual unit operations include: (1) sludge concentration, (2) sludge oxidation, (3) phase separation, (4) sludge dewatering, and (5) off-site pyrometallurgical metal recovery. The unit operations in dashed-line boxes are optional treatments to recover metals from the aqueous stream from the phase separation unit. These treatments include (1) pretreatment (granular media and activated carbon filtration and pH adjustment), (2) ion exchange, and (3) off-site metal recovery from the ion exchange regenerate solution.

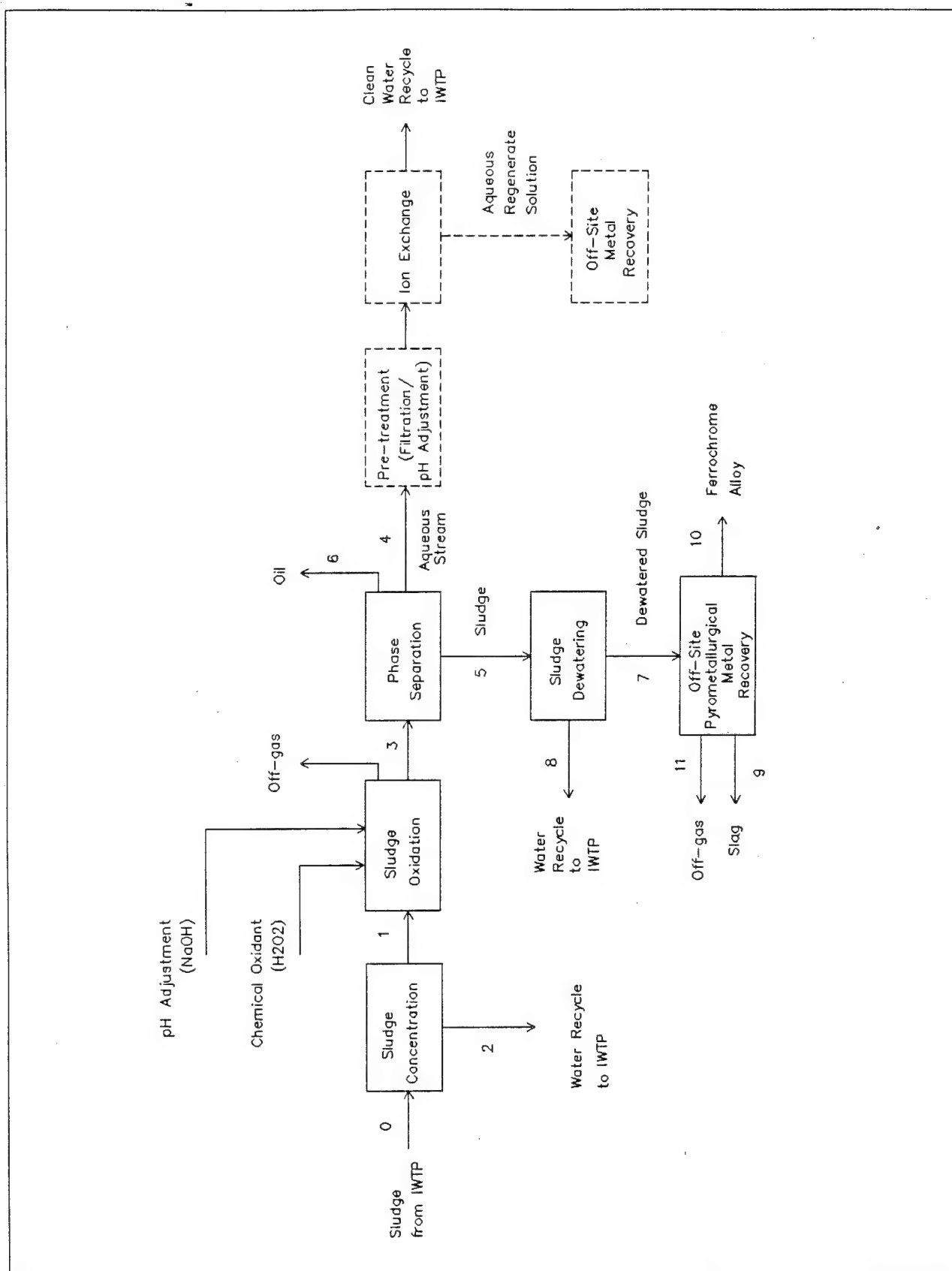


Figure 8. Process Block Diagram.

- a. Sludge Concentration

The feed sludge is first introduced in a sludge concentration unit. Three feasible options for concentrating the sludge have been identified—froth flotation, gravity settling, and centrifugation.

In froth flotation, a frothing agent is added to the wastewater and air bubbles rising to the surface carry solid particles that are attached to the liquid-air interface of the bubble. To remove the solid material from the wastewater, the froth is skimmed or drained off the top of the water.

Using a settling process, natural sedimentation of the solids is allowed to occur and then the concentrated sludge is pumped from the bottom of the tank. Any solids that float due to coating by organic materials may be removed by skimming, if necessary.

In centrifugation, solids are continuously separated from water by applying mechanical centrifugal force. Sludge and water are then removed as separate streams.

With all of the above methods, the water removed from the sludge would be recycled to the IWTP. The foam or sludge containing the metal sulfides, organics, and inert solids is then pumped to the oxidation unit.

b. Sludge Oxidation

Oxidation of the sludge will be achieved by one of three possible methods—electrolytic oxidation, hydrogen peroxide oxidation, or wet air oxidation. Each of these methods will oxidize the metal sulfides to metal sulfates. Some of the metal sulfates are very soluble in water and, therefore, will be separated with the water. Other metals will form hydroxide, oxide, and sulfate precipitates and will be removed with the sludge.

In the electrolytic oxidation unit, an electrolyte, sodium chloride (NaCl), would be added to facilitate the formation of chlorine at the

anode and sodium hydroxide at the cathode. The chlorine is hydrolyzed by the water to form hypochlorous acid (HOCl) and hydrochloric acid. The hypochlorous acid is the active species for oxidation of sulfide to sulfate. Based on laboratory tests, the feed solution must be at least 1 percent NaCl for oxidation to occur at an acceptable rate. During electrolytic oxidation, the pH of the sludge drops. Without control of the pH, some of the sulfides may be converted to sulfur and precipitate with the sludge solids. Sulfur in the sludge can interfere with the pyrometallurgical metal recovery process and needs to be avoided. Adding sodium hydroxide (NaOH) to the sludge in the oxidation tank will control pH. The amount of NaOH required will depend on the oxidation process and can be varied during pilot-scale tests to determine the optimum operating pH.

In the hydrogen peroxide oxidation unit, hydrogen peroxide (H_2O_2) solution would be added to the sludge to obtain chemical oxidation of the metal sulfides to metal sulfates. Concentrated H_2O_2 would be added to obtain 4 percent by weight total H_2O_2 concentration in the sludge. Lower overall concentration of the chemical in the sludge will also provide oxidation, but at a slower rate. Trade-offs between reaction time and costs for H_2O_2 would be investigated during pilot-scale testing.

In a wet air oxidation unit, high pressure (approximately 2000 psi) and high temperature (approximately 280°C) are used to oxidize the sulfide to sulfate and to decompose approximately 80 percent of the organics to carbon dioxide and water.

In summary, the major technical differences between the three oxidizing processes are the methods of oxidizing the sludge, the nature of the additives, the nature of the effluent streams, and the extent of oxidation of the organic materials in the sludge. Cost evaluations will be required to help determine the most appropriate oxidation unit for the treatment facility. The output of the oxidation unit will be sent to a phase separation unit where the solution, the organics, and the solid residues are separated.

- c. Phase Separation

During the oxidation process, organics and water are released from the sludge solids. The water joins the water in the separator, the other two phases will be allowed to separate by gravity in a phase separation unit. The lighter oil/grease phase will be skimmed from the top of the unit and collected in a drum or combined with the oil/grease skimmings from the separator that precedes the chromium reduction unit. The aqueous phase will be recycled to the IWTP or treated in a dedicated ion exchange unit. For the purpose of this evaluation, it is assumed that the aqueous stream can be recycled to the IWTP without further treatment. The solids that have settled on the bottom of the phase separation unit will be pumped to the sludge dewatering unit.

d. Sludge Dewatering

Sludge dewatering will be accomplished in a batch operation using a basket-type centrifuge. A holding tank will be used to store sludge until centrifugation. This process would produce a cake of sludge that will be sent to an off-site pyrometallurgy vendor facility for metal recovery. The water will be removed and recycled to the IWTP.

e. Pyrometallurgical Metal Recovery

Due to large capital costs and limited time, pilot-scale tests of a pyrometallurgical metal recovery process are best provided at an off-site vendor facility. In a pyrometallurgy furnace, the sludge will be heated to temperatures that will vaporize the residual water and low melting point metals (cadmium, zinc, lead, etc.), and also decompose any residual organics and sulfates to their oxide gases. The inerts will slag off the top of the melt and ferrochrome ingots will be produced for use in the manufacture of alloys. Off-gases from this process are treated for release to the atmosphere. According to vendors of pyrometallurgical facilities, the slag that results from this process can be disposed of as a nonhazardous, solid waste.

f. Optional Treatment

The aqueous stream from the phase separation process may be returned to the IWTP or treated further in an ion exchange system. The solutions from regeneration of the ion exchange beds can then be treated at an off-site hydrometallurgical facility. The benefits of treating this aqueous stream include recovering more metals from the sludge and avoiding recycling metal ions to the IWTP. Some of the metals in the sludge are solubilized during the oxidation process, and without further treatment of the aqueous stream, are recycled to the IWTP.

2. Mass Flow Simulation

To assist in estimating equipment sizes and to help provide an overall view of the pilot plant process, the total process was simulated on ASPEN process simulation program. The performance of each unit was based on the laboratory studies conducted during the first stages of this program and on vendor data. The primary purpose of these material balances was to determine flow rates and compositions to be used in equipment sizing and selection and not to precisely determine the actual expected stream compositions.

The ASPEN/SP computer code, developed by Simulation Sciences Inc., is a commercially available computer code that performs process simulation for a wide range of chemical systems. Applications of ASPEN/SP include: chemical production and handling, oil and gas production and refining, coal fuels, synthetic fuels, pulp and paper, power generation, metals processing, cryogenics, waste treatment, and food processing, among others.

For this work, ASPEN/SP was used to perform material balance and case study calculations for the sludge treatment process. Calculations were done for several scenarios, wherein the overall concentration of solids in the feed was varied, and the effect of added NaCl, H₂O₂, or organics was studied. ASPEN/SP simulated the various chemical component splits that were specified for each unit operation, such as those for a filter, clarifier, etc. Such simulations allow

for accurate record keeping of a given chemical component throughout the entire treatment process.

The performance of the three different sludge concentration units was assumed to be the same and, therefore, variations to the overall mass balance due to performance of these units were neglected. Differences in the three oxidation units required three different mass balances to be performed. The mass balances of the system using each of the three oxidation units are shown in Tables 19, 20 and 21. (In these mass balance tables, two figures are given in some data blocks; the upper figure is for a sludge of 0.3 percent solids and the lower figure is for 1.0 percent solids sludge.) The optional ion exchange treatment of the aqueous stream from the phase separation unit was not included in the simulation or in the cost estimates.

The performance parameters and assumptions used in the ASPEN simulation for each unit are listed below.

- Sludge concentration:
 - 90 percent of the solids are removed by flotation—10 percent of the solids remain in the water to be returned to the IWTP.
 - The maximum concentration of the concentrated sludge is 5 percent solids, by weight, in the sludge concentrate.
 - 10 percent of the water in the sludge will leave the unit with the flotation froth.
- Oxidation
 - 100 percent of the sulfides are oxidized to sulfates.
 - 0.1 percent water, inerts, and metals remain in the oil/grease.

TABLE 19. MATERIAL BALANCE FOR PROCESS USING AN ELECTROOXIDATION UNIT.

Stream Number Components	0	1	2	3	4	5	6	7	8	9	10	11
Mass Flow (Kg/day)	18982 19116	1944 3441	17038 15675	2045 3618	1709 2410	325 1168	10.8 39.4	36.1 129.8	289 1038	31 112	4 14	4 13
Mass Flow Influent (Kg/day)				102 181								
% Suspended Solids (Wgt %)	0.3 1.0	2.64 5.00	0.03 0.12	2.43 4.58	0.39 0.47	10		90	0			
% Metal Sulfide of SS (Wgt %)	20 20	20 20	20 20	18 18	42 42	18.8 21.4		18.8 21.4	0 0			
% Organic of SS (Wgt %)	25 25	25 25	25 25	26 26	29 29	0.4 0.4		0.4 0.4	0			
% Inerts of SS (Wgt %)	55 55	55 55	55 55	56 56	29 29	81.8 78.2		81.8 78.2	0 0			
Dissolved Ions												
Fe ($\mu\text{g/g}$)	0.395	0.395	0.395	2.200	2.200	2.200			2.200			
Cr ($\mu\text{g/g}$)	0.076	0.076	0.076	4.500	4.500	4.500			4.500			
Cd ($\mu\text{g/g}$)	0.001	0.001	0.001	0.210	0.210	0.210			0.210			
Pd ($\mu\text{g/g}$)	0.002	0.002	0.002	0.030	0.030	0.030			0.030			
Ni ($\mu\text{g/g}$)	0.016	0.016	0.016	5.100	5.100	5.100			5.100			
Other ($\mu\text{g/g}$)	0.040	0.040	0.040	6.600	6.600	6.600			6.600			
SO ₄ ($\mu\text{g/g}$)	0.000 0.000	0.000 0.000	0.000 0.000	3433 9972	3433 9972	3433 9972			3433 9972			
Na ($\mu\text{g/g}$)	0.000 0.000	0.000 0.000	0.000 0.000	11.97 15.03	11.97 15.03	11.97 15.03			11.97 15.03			

TABLE 20. MATERIAL BALANCE FOR SYSTEM USING A HYDROGEN PEROXIDE UNIT.

Stream Number Components	0	1	2	3	4	5	6	7	8	9	10	11
Mass Flow (Kg/day)	18982 19116	1944 3441	17038 15675	2226 3914	1890 2707	325 1168	10.8 39.4	36.1 129.8	289 1038	31 112	4 14	4 13
Mass Flow Influent (Kg/day)				283 478								
% Suspended Solids (Wgt %)	0.3 1.0	2.64 5.00	0.03 0.12	2.23 4.23	0.35 0.42	10		90	0			
% Metal Sulfide of SS (Wgt %)	20 20	20 20	20 20	18 18	42 42	18.8 21.4		18.8 21.4	0 0			
% Organic of SS (Wgt %)	25 25	25 25	25 25	26 26	29 29	0.4 0.4		0.4 0.4	0			
% Inerts of SS (Wgt %)	55 55	55 55	55 55	56 56	29 29	81.8 78.2		81.8 78.2	0 0			
Dissolved Ions												
Fe ($\mu\text{g/g}$)	0.395	0.395	0.395	2.200	2.200	2.200			2.200			
Cr ($\mu\text{g/g}$)	0.076	0.076	0.076	4.500	4.500	4.500			4.500			
Cd ($\mu\text{g/g}$)	0.001	0.001	0.001	0.210	0.210	0.210			0.210			
Pd ($\mu\text{g/g}$)	0.002	0.002	0.002	0.030	0.030	0.030			0.030			
Ni ($\mu\text{g/g}$)	0.016	0.016	0.016	5.100	5.100	5.100			5.100			
Other ($\mu\text{g/g}$)	0.040	0.040	0.040	6.600	6.600	6.600			6.600			
SO ₄ ($\mu\text{g/g}$)	0.000 0.000	0.000 0.000	0.000 0.000	3104 8879	3104 8879	3104 8879			3104 8879			
Na ($\mu\text{g/g}$)	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000			0.000 0.000			

TABLE 21. MATERIAL BALANCE FOR PROCESS USING A WET AIR OXIDATION UNIT.

Stream Number Components	0	1	2	3	4	5	6	7	8	9	10	11
Mass Flow (Kg/day)	18982 19116	1944 3441	17038 15675	1932 3402	1606 2228	326 1169	0.5 4.9	36.0 130.0	289 1039	31 112	4 14	4 13
Mass Flow Influent (Kg/day)				27 26								
% Suspended Solids (Wgt %)	0.3 1.0	2.64 5.00	0.03 0.12	2.05 3.90	0.41 0.51	10		90	0			
% Metal Sulfide of SS (Wgt %)	20 20	20 20	20 20	23 23	42 42	18.8 21.5		18.8 21.5	0 0			
% Organic of SS (Wgt %)	25 25	25 25	25 25	6 6	29 29	0.4 0.4		0.4 0.4	0			
% Inerts of SS (Wgt %)	55 55	55 55	55 55	71 71	29 29	81.8 78.1		81.8 78.1	0 0			
Dissolved Ions												
Fe ($\mu\text{g/g}$)	0.395	0.395	0.395	2.200	2.200	2.200			2.200			
Cr ($\mu\text{g/g}$)	0.076	0.076	0.076	4.500	4.500	4.500			4.500			
Cd ($\mu\text{g/g}$)	0.001	0.001	0.001	0.210	0.210	0.210			0.210			
Pd ($\mu\text{g/g}$)	0.002	0.002	0.002	0.030	0.030	0.030			0.030			
Ni ($\mu\text{g/g}$)	0.016	0.016	0.016	5.100	5.100	5.100			5.100			
Other ($\mu\text{g/g}$)	0.040	0.040	0.040	6.600	6.600	6.600			6.600			
SO ₄ ($\mu\text{g/g}$)	0.000 0.000	0.000 0.000	0.000 0.000	3661 10807	3661 10807	3661 10807			3661 10807			
Na ($\mu\text{g/g}$)	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000	0.000 0.000			0.000 0.000			

- 0.1 percent organics, inerts, and metals remain in the water
- The oxidized sludge contains 1 percent of the organics originally found in the sludge, 99.8 percent of the original metals, and 99.8 percent of the original inerts.
- In the electrolytic oxidation unit, 20 percent by weight NaCl solution is added, and enough solution is added to achieve 1 percent NaCl in the sludge.
- In the hydrogen peroxide oxidation unit, 30 percent by weight reagent hydrogen peroxide solution is added, and enough solution is added to achieve 4 percent H_2O_2 in the sludge.
- In the wet air oxidation unit, the organic concentration in the feed sludge must be at least 20 gallon/liter a fuel must be added to raise the concentration, and 80 percent of the organics will be decomposed to carbon dioxide and water.

- Phase Separation

- The unit provides 100 percent separation of the oil/grease phase from the aqueous phase.
- The unit separates 100 percent of the aqueous phase from the sludge.
- The sludge leaving this unit is 10 percent solids and 90 percent water by weight.

- Sludge Dewatering

- The sludge dewatering unit results in a sludge that is 70 percent solids and 30 percent water by weight.

• Pyrometallurgical Metal Recovery

- The pyrometallurgy unit provides 100 percent vaporization of water into steam.
- 100 percent separation of ferrochrome alloy.
- 100 percent transfer of other metals into slag.

3. Cost Estimates

a. Equipment

Equipment size and cost estimates for the various unit operations have been made. These estimates are based on the results of the process testing performed during the earlier phases of this project, vendor data, periodical information, and textbook and handbook information. These are rough order-of-magnitude estimates.

Appendix B contains tables of size and cost estimates for the major pieces of equipment, along with some auxiliary equipment, for all of the proposed unit operations. Table 22 summarizes the estimated equipment costs.

The nine process options listed in Table 22 include the possible combinations of the three options for initial dewatering of the sludge and the three for oxidation. All nine options include the same phase separation unit, sludge dewatering, and pyrometallurgical metal recovery process. For example, option 1 consists of a froth flotation unit for dewatering the sludge, an electrolytic oxidation unit, a gravity phase separator, a centrifuge, and pyrometallurgical metal recovery. Option 2 consists of a centrifuge, an electrolytic oxidation unit, a gravity-phase separator, a centrifuge, and pyrometallurgical metal recovery.

TABLE 22. ESTIMATED EQUIPMENT COSTS IN THOUSANDS OF DOLLARS.

Options	1	2	3	4	5	6	7	8	9
Sludge Concentration									
•Froth Flotation	27.7			27.7			27.7		
•Centrifuge		51.8			51.8			51.8	
•Settling Tank			18.5			18.5			18.5
Oxidation									
•Electro-oxidation	37.5	37.5	37.5						
•H ₂ O ₂ Oxidation				4.8	4.8	4.8			
•Wet Air Oxidation							2,500.0	2,500.0	2,500.0
Separation	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8
Dewatering	26.0	26.0	26.0	26.0	26.0	26.0	26.0	26.0	26.0
Pyrometallurgy	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
TOTAL	197.0	221.1	187.8	164.3	188.4	155.1	2,659.5	2,683.6	2,650.3
Note: Pyrometallurgy cost (\$100,000) is the estimated cost of pilot-scale evaluation of pyrometallurgical metal recovery technology by an off-site vendor.									

Because of significantly higher equipment costs for wet air oxidation versus other oxidation alternatives, Options 7, 8, and 9, were omitted from further analysis. Operating costs may also be high for wet-air oxidation, depending on the fuel value of the sludge.

It may be observed from the data in Table 22, that Options 1 through 6 are nearly equal in capital costs. An annual operating cost analysis is needed to determine which option will be least expensive over a given process lifetime. This analysis is discussed in the following sections.

b. Annual Maintenance and Operation Costs

Estimated annual maintenance and operation costs include utilities, chemicals, labor, and materials. These costs were calculated separately and totalled in Table 23. Due to the complexity and variability of the system, maintenance and operation estimates for the pyrometallurgical process were not calculated.

Utilities required by the metals recovery pilot plant include electricity, water, and compressed air. Power at 110 VAC is available at the existing pilot plant facility and will run most of the equipment. However, an electrolytic oxidation unit would use low-voltage DC power, and a rectifier would be needed to convert AC power to DC. The water required for NaCl or H_2O_2 solutions is available for this project. An air compressor for the diaphragm sludge pumps will be rented from a local equipment supplier in the area of Tinker AFB for pilot-plant testing, and may be purchased for implementation of the final process. The total utility costs have been estimated for options 1 through 6 and are included in Appendix B. (Note: Options 7, 8 and 9 were eliminated from further analysis in the previous section due to high capital costs.)

Chemicals required for the pilot plant may include methyl isobutyl carbinol (MIBC) for froth flotation, H_2O_2 for hydrogen peroxide oxidation, NaOH for pH adjustment, and NaCl for electrolytic oxidation. The estimated costs for these chemicals can be found in Appendix B and are included in the cost summary of Table 24.

TABLE 23. ESTIMATED COSTS FOR THE SLUDGE TREATMENT PILOT PLANT OPTIONS.

<u>Process</u>	<u>Option</u>	<u>Equipment cost</u>	<u>Maintenance and operation costs</u>
Sludge concentration	Froth Flotation	\$ 27,200	\$ 32,890
	Centrifuge	\$ 51,800	\$ 19,710
	Settling Tank	\$ 18,500	
Oxidation	Electrooxidation	\$ 25,500	\$ 252,895
	H ₂ O ₂ oxidation	\$ 4,450	\$ 254,425
	Wet air oxidation	\$ 2,500,000	Not Available
Oil/Water/Sludge Separation Unit	-	\$ 5,800	\$ 180
Centrifuge	-	\$ 26,000	\$ 3,905
Pyrometallurgical Smelting Unit Tests	-	\$ 100,000	Included in Testing Cost

TABLE 24. CHEMICAL COSTS.

<u>Chemical</u>	<u>Price</u>	<u>Amount Used/day</u>	<u>Cost/day</u>
MIBC	\$1.00/lb	1 lb/day	\$ 1
NaCl	\$0.50/lb	78 lb/day	\$ 39
H ₂ O ₂	\$4.50/gal	3 gal/hr	\$324

Appendix B contains details on the labor and material costs of maintenance and operation. Labor and materials for process control, preventative maintenance of the equipment, and calibration of the instruments are included in this estimate. Labor costs were based on a rate of \$50/hour.

c. Monitoring and Control Systems

During the early phases of the pilot-scale tests, most monitoring and control of the process will be performed manually. Minimal instrumentation will be needed for manual control of the process, and instrumentation costs are included with equipment cost estimates. Automation of the process will minimize operator time and simplify operation of the plant, but uncertainties in the overall treatment process make development of these systems

impractical at this time. During the more advanced stages of the pilot-scale tests, automatic monitoring and control systems will be incorporated.

4. Pilot Plant Facility

a. Facility Description

The pilot plant will be set up in an existing facility at Tinker AFB. The facility was built in FY 90 around the Tinker field demonstration IWTP system for housing pilot-scale waste treatment tests. The building measures approximately 56 feet x 24 feet x 12 feet. It is equipped with the environmental controls necessary to allow research and operation of the pilot plant without interruption due to weather conditions. A 12 x 56-foot trailer to accommodate analytical equipment is attached to this building.

The floor of the facility is concrete and is curbed and sloped to three floor drains that return liquids to the IWTP. The doorways have thresholds to make a water-tight dam across the door openings. There are three standard doors and one 8-foot x 10-foot overhead rollup door for bringing large equipment into the facility. A gravel road leads to the rollup door.

Three-phase power (440 volts) is delivered to the facility and is routed to an exhaust fan, heaters, and a transformer. The transformer converts the three-phase power to 208-volt three-phase power and 110-volt single-phase power that is routed to ten 110-volt receptacles. Battery-powered emergency lights have also been installed in the facility per OSHA requirements.

More detailed specifications of the demonstration facility are listed in Reference 2.

b. Chemical Storage

There are no special chemical storage needs for this project. MIBC, NaCl, H₂O₂, and NaOH can be stored in their shipping containers. The thickened, oxidized sludge and the oil pumped from the phase separation unit will

be collected in 55-gallon drums during the process tests. Full drums will be stored in the facility until the sludge is sent offsite for further testing and the oil to be recycled. Waste water will be returned to the IWTP through the drains in the floor of the facility.

5. Safety and System Compatibility Considerations

a. Safety

Aside from standard safety precautions involved with running any industrial facility, additional precautions must be taken when working with chemicals and high current electricity. Items of possible concern for this pilot plant include the use of H_2O_2 , NaOH, and electricity, and the generation of chlorine gas.

Hydrogen peroxide (H_2O_2) in concentrations of 35 percent and greater can easily cause blistering of the skin and in concentrations of above 52 percent, the rapid decomposition of H_2O_2 to water and oxygen can generate enough heat to boil off all of the water in the solution. This results in a very large increase in volume and can rupture containers or piping. Loss of water due to evaporation will cause the concentration of the solution to increase, which will increase the potential for a fire. The use of vented containers to reduce evaporation of water is recommended for storing H_2O_2 . A vent in the container will prevent pressurization of containers from decomposition of the chemical into water and oxygen. To minimize any risks to workers, 30 to 35 percent by weight solution hydrogen peroxide will be used and appropriate training on handling procedures will be provided to operating personnel. Material Safety Data Sheets (MSDSs) will be available to all personnel in the plant.

Methods for safe handling of NaOH include: segregated storage, use of compatible materials for storage and use, availability of eye washes, and worker awareness of proper handling and safety procedures.

Other chemicals possibly required for the operation include MIBC (a frothing agent) and NaCl (table salt). These chemicals pose minimal safety concerns, and MSDSs will be provided to those working in the facility.

Electricity and water pose a potential electrocution hazard, and must be considered in the operation of an electrolytic oxidation unit. Preliminary design calculations for an electrolytic oxidation unit indicate currents as high as 2000 amps, depending on flow rate, concentration, time allowed for reaction, and the configuration of the anode and cathode plates. Engineering controls and proper operating instructions are required for a safe operation.

In the electrolytic oxidation process, no hazardous chemicals are added (only NaCl solution) but chlorine gas is formed at anode. This chlorine reacts with the water about as rapidly as it is generated to form hypochlorous acid, HOCl. An automatic chlorine gas monitor should be provided to warn operators of excessive chloring levels during pilot-scale tests and additional ventilation or an off-gas treatment system may be required. Termination of the power to the unit will stop the reactions, so the process can be terminated almost instantly in the event of an emergency.

b. System Compatibility

As an integrated part of the overall IWTP system, one important requirement of the metals recovery process is that it does not interfere with other processes in the IWTP. Because water from this treatment process will be recycled to the IWTP, this requirement must be considered whenever the sludge is altered or materials are added to it. The addition of MIBC (a frothing agent) and/or H_2O_2 may be a concern and their affect on the IWTP must be considered.

MIBC was previously found to improve the performance of froth flotation. While the chemical would only be added in small quantities, any of the frothing agent that may reach the activated sludge system, which treats the overflow of the SCC, may cause excessive foaming in the aeration basins and

interfere with the process. For this reason, frothing agents will not be used in the metals recovery process.

Minor concerns over compatibility of the metal recovery system with the IWTP also exist with the use of H_2O_2 . The by-products from the decomposition of the chemical are water and oxygen, neither of which would impact the normal operations of the IWTP. If not completely decomposed, H_2O_2 may have an adverse affect on the activated sludge treatment process. Although decomposition of the chemical before reaching this system is expected, the streams recycled to the IWTP will be monitored for H_2O_2 .

During laboratory testing it was noted that frothing due to oxygen release occurs on too rapid addition of H_2O_2 to the sludge. To avoid any problems with addition of the chemical, it will be added in-line directly before the oxidation unit and the rate of addition will be monitored closely. To prevent pressure increases, the tank must be open to the atmosphere. Compatibility of equipment materials must also be considered for the tank, the lines, and the pumps.

6. Evaluation and Conclusion

During this economic analysis, three methods for initial concentration of the sludge and three methods for oxidation of the sludge were considered. The amounts of ferrochrome product and slag produced are independent of which options are chosen for these unit operations.

Comparing the output of the sludge concentration options, only the amount of water removed from the sludge varies. The amount of water in the sludge affects the volume of the sludge and, therefore, the size of the oxidation and phase separation units. This implies a trade-off between the cost of an initial concentration unit and size (and probably cost) of the oxidation and phase separation units. However, at the relatively low flow rates of this waste stream, the equipment costs are not particularly sensitive to increases in volume.

Comparing the output of the sludge oxidation options, the amount of water to be recycled to the IWTP or processed through an ion exchange system, the amount of oil/grease released or destroyed, and the amount of sodium ion and sulfate ion in solution are affected by the option selected. The difference in the amount of water is a result of the water in the H_2O_2 solution that is added during chemical oxidation of the sludge. This increase in water causes the difference in the concentration of the sulfate ion in the water streams. A decrease in the organic material occurs only from the conversion of oils and greases to carbon dioxide and water during the high-temperature, high-pressure oxidation in the wet-air oxidation unit. The increase in sodium ions in solution is a result of the addition of NaCl in the electrolytic oxidation unit.

The equipment costs indicate that the least expensive option involves the use of a settling tank and a hydrogen peroxide oxidation unit. Annual operating costs are also lower for this option.

SECTION IV
PHASE III RESULTS

A. TASK 5. ENGINEERING DESIGN FOR PILOT FIELD DEMONSTRATION UNIT

1. Functional and Operational Requirements

Functional and operational requirements for the pilot-scale sludge treatment process are described below.

a. Functional Requirements

- The process will be capable of treating up to 5000 gallon/day of industrial sludge from Tinker IWTP SCC.
- The sludge will be treated to produce residuals that are nonhazardous, or at least minimized in volume, in an economical and practical manner.
- The process will produce a sludge that can be treated economically by pyrometallurgical processes to produce reusable ferrochromium alloy by removing sulfides and organic materials from the sludge, if possible.

b. Operational Requirements

- Operation of the metals recovery process will not cause upset of the other treatment processes within the IWTP due to recycled chemical additives or contaminants.
- The operational complexity of the process shall be consistent with typical industrial wastewater treatment operations to the extent possible.

- The process will be capable of continuous operation.
- The process will be designed to minimize the exposure of operating personnel to hazardous chemicals.
- The process will be designed to prevent environmental impact due to system failure (e.g., containment leaks, power failure).
- In the event of power failure, system must shut down in fail-safe condition.

2. Technology Assessment

Several alternatives for treating the sludge were identified during the research and testing phase of this project including chemical precipitation, ion exchange, electrowinning, electrodialysis, wet-air oxidation, and electrochemical incineration. Among the conclusions from these studies were that separation of the metals from the sludge was possible and that removal of sulfide and organic contaminants would render the sludge more amenable to metal recovery. The technologies remaining after initial screening for technical feasibility and cost are discussed in the following sections. A final recommendation is made for the process to be pilot tested.

a. Recommended Process for Pilot-Scale Testing

The estimated costs for the different unit operations considered for pilot-scale testing are given in Table 25. Technical assessment of each alternative follows.

(1) Sludge Concentration Unit

The three technologies considered for concentration of the sludge were froth flotation, centrifugation, and gravity settling. Each of

these alternatives is technically feasible and will concentrate the sludge solids, reducing the volume of sludge which must be treated.

TABLE 25. ESTIMATED COST OF PILOT PLANT FACILITY.

Engineering, design, inspection	\$ 27,200
Equipment costs	155,100
Installation costs (35 percent of equipment)	54,300
Construction costs subtotal	209,400
Project administration costs (4 percent of construction)	8,400

Subtotal	245,000
Contingency (19 percent of subtotal)	
46,600	
	=====
Total estimated cost to construct	\$291,600

With froth flotation, there is some concern that the use of additives to enhance the performance could interfere with the operation of the full-scale activated sludge system. Water recovered from the sludge treatment process will be recycled to the IWTP. Therefore, low levels of frothing additives will be recycled to the activated sludge system and could interfere with the process. Froth flotation has been shown to be effective without the use of frothing additives.

While a centrifuge can produce a higher concentration of solids than gravity settling or froth flotation, the superior performance does not justify the significantly higher capital and maintenance costs associated with a centrifuge. Table 25 indicates that the initial costs and periodic maintenance costs for gravity settling and froth flotation are significantly lower than those for a centrifuge. While the performance of both centrifugation and froth flotation are better, gravity settling is recommended for the sludge concentration step because of the low capital and operating costs, the simplicity of the operation, and because the extent of sludge concentration is not critical to the overall process.

(2) Oxidation Unit

The technologies considered for oxidation of the sludge include electrolytic oxidation, chemical oxidation using hydrogen peroxide (H_2O_2), and wet-air oxidation. The purpose of the oxidation step is to convert the insoluble metal sulfides in the sludge to soluble metal sulfates. This enables the sulfates to be removed from the sludge with the aqueous phase during the phase separation step.

Upon oxidation of the sulfides, some of the metals form low solubility oxide and hydroxide precipitates, e.g., $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$. Low solubility metal sulfates such as $PbSO_4$ and $BaSO_4$ may also be present in the precipitate. Other metals such as nickel and cadmium would be present in solution as their sulfate salts.

The oxidation process will also free oils and greases from the sludge and allow a separate liquid hydrocarbon phase to form. Many of the commercial metal reclaimers contacted indicated limits to the amount of organic materials and sulfur that their processes could handle. By removing sulfur and oils and greases, the sludge can be accepted by a greater number of metal reclaimers.

Wet-air oxidation is a high-pressure, high-temperature process in which sulfides and organic materials are oxidized in an aqueous phase. Due to the need for a pressure vessel and expensive materials of construction, the cost of this process is much higher than the alternatives (see Table 25). Therefore, wet air oxidation is not recommended for treatment of the metal sulfide sludge. Although not considered as part of this study, wet-air oxidation may be more suitable for treatment of the biological sludge or a combination of the metal sulfide and biological sludge generated at Tinker AFB. The volume of biological sludge is significantly larger than that of the metal sulfide sludge. It is expected that a large reduction in volume of the biological sludge could be achieved by wet air oxidation.

Both electrolytic and hydrogen peroxide oxidation are technically promising alternatives. While operating costs of the two options are comparable, the capital and maintenance costs are much higher for an electrolytic oxidation unit (see Table 25). Other factors to be considered in selecting a process are implementability and flexibility. The hydrogen peroxide unit is an uncomplicated system that involves few process variables and can be easily installed and verified. The electrolytic oxidation system is much more complicated and will require more testing and optimization to effectively implement than would a hydrogen peroxide unit. There is some concern as to how very high or low solids concentrations would affect the performance of electrolytic oxidation. The hydrogen peroxide process can be easily adjusted for variations in sludge composition, while the nature of the electrolytic oxidation unit makes adjustments difficult and expensive.

(3) Phase Separation Unit

Much of the organic material and water in the sludge will be freed from the sludge solids as a result of the oxidation process. The liquid organic (hydrocarbon), aqueous, and sludge phases can be separated by gravity separation methods. The liquid organic phase will be skimmed from the liquid surface and collected in drums for disposal or recycling. The sludge will be pumped from the bottom of the tank, dewatered in a batch operation, and collected for further processing.

The aqueous phase will be treated for removal of the soluble metal species and recycled to the IWTP. This can be accomplished by treatment in a dedicated ion exchange system which would include pretreatment by granular media and activated carbon filtration. As an alternative this stream could be directed to the full-scale ion exchange system which was recommended in a previous study to polish the IWTP effluent. This system has not yet been installed.

A cone-bottom tank with a three-baffle phase separation system or with a floating oil skimmer would be an inexpensive and appropriate solution for the phase separation step. A pilot-scale Solids Contact Clarifier

already exists at the IWTP pilot plant facility and, if adequate, may be used in this service.

(4) Dewatering Unit

The treated sludge must be further dewatered before shipment to an off-site pyrometallurgical process vendor for demonstration tests. These vendors can accept only limited quantities of hazardous material for testing; dewatering the sludge will increase the solids concentration of sludge to be sent off-site and less water will be included as hazardous material. A basket-type centrifuge operating in a batch mode is recommended for this service. The water removed from the sludge will be recycled to the IWTP.

(5) Pyrometallurgy Process

A pyrometallurgical process is recommended to recover a ferrochromium alloy from the dewatered sludge and to produce a nonhazardous slag by-product. Several metal reclaimers were contacted for this purpose and each had different requirements for the sludge characteristics, particularly sulfur and organic content.

At least one vendor with suitable process technology has been found that can test samples of the dewatered sludge at their facility to determine process performance and characteristics.

b. Alternative Pilot Plant Design

As an alternative to sludge pretreatment by the process described above, it may be possible to treat dewatered SCC sludge directly in a pyrometallurgical process to recover ferrochromium alloy. While vendors of these pyrometallurgical technologies typically will not accept metal sulfide sludges containing sulfur, organic, and/or other contaminants which exceed maximum concentration limits, one vendor has stated that they will accept Tinker AFB metal sulfide sludge for testing based on the characterization determined in Phase II. This alternative could be evaluated by sending a sample of dewatered

SCC sludge to this vendor for testing. This could be done instead of the pilot-scale testing of the process described above or in parallel with the pilot-scale testing.

3. Design Basis

a. Feed Stream Characteristics

The design of the sludge treatment pilot plant shall be based on an SCC sludge underflow rate of 5000 gallons/day. Sludge solids content has been reported to vary between 0.3 and 8.4 percent; 0.3 to 1.0 percent solids will be used for design of the pilot plant. The design composition of the dry sludge solids are given in Table 26. Preliminary equipment sizing and cost estimates prepared for this report were based upon a ten to one sludge volume reduction in the sludge concentration step, which yields a flow rate of 500 gallons/day of concentrated sludge to the oxidation step. This assumption will be evaluated further as the design proceeds as it may affect final equipment sizes and costs. These values are taken from EG&G Idaho internal correspondence.*

b. Key Design Assumptions

Other key assumptions to be used in the design of the pilot plant include:

- Minimum of 2 percent solids in sludge from sludge concentration step
- 100 percent oxidation of sulfides to sulfates
- 100 percent separation of hydrocarbon phase from aqueous phase following oxidation step.

* W. F. Bauer "Analysis of Sludge Samples," interoffice correspondence to R. L. Miller, December 17, 1990, WFB-26-90.

TABLE 26. COMPOSITION OF DRY SCC SLUDGE SOLIDS TO BE USED IN PILOT PLANT DESIGN.

<u>Constituent</u>	<u>percent(w/w) in dry sludge solids</u>
Oil and grease	25
Iron	2.5
Chromium	3.2
Cadmium	0.046
Lead	0.052
Nickel	0.37
Manganese	0.33
Copper	0.053
Aluminum	1.0
Barium	0.25

c. Design Codes and Standards

A preliminary list of applicable design codes and standards has been prepared for design and operation of the pilot plant facility. The codes and

standards identified at this time are listed below. This list will be reviewed and updated prior to construction of the pilot plant.

- Code of Federal Regulations (References 20-22)
- General Reference Codes (References 23-27)
- U.S. D.O.D., U.S. Air Force, and Applicable SM-ALC Codes and Standards

4. Process Description

a. General

The sludge treatment process selected in the Technology Assessment section of this report consists of six steps, four of which will be demonstrated at pilot scale at Tinker AFB (see Figure 9). The first step is

gravity settling to increase the solids concentration of the sludge. The second step is oxidation of the concentrated sludge solids with hydrogen peroxide to oxidize sulfide to soluble sulfate and to allow a separate liquid hydrocarbon phase to form. The third step is a gravity-phase separation in which liquid hydrocarbon, aqueous, and sludge phases are separated. The hydrocarbon phase is collected for disposal or recycle. The aqueous phase containing the soluble metal sulfate ions may be recycled directly to the IWTP or be treated by ion exchange to remove the metal ions and then recycled back to the IWTP. The sludge phase is treated in the fourth process step, sludge dewatering, in which the sludge is dewatered to produce an acceptable feed for the pyrometallurgical process step. In the pyrometallurgical step, ferrochromium alloy is recovered from the sludge. This final process step will be demonstrated off-site at a vendor facility.

Sludge will be pumped from the IWTP SCC underflow to the pilot plant using a diaphragm or progressive cavity-type pump and a new transfer line. The transfer line may be either a permanent buried line or temporary above-ground flexible hose or tubing. A sludge feed storage tank may also be provided at the pilot plant to facilitate batch-type operations during the optimization portion of the testing. All liquid effluents from the pilot plant will drain to an existing adjacent lift station and be pumped back to the IWTP.

b. Sludge Concentration Unit

The SCC sludge will enter the pilot plant at the gravity settler (thickener) (see Figure 9). The settler will be a cone-bottom tank of sufficient diameter and residence time to allow for solids settling. Capability will be provided to vary the feed rate to the settler to determine the effect of residence time on performance. This may be accomplished by either diverting a portion of the flow to a floor drain or by using a variable speed feed pump. Clarified liquid will overflow from the settler to a floor drain and be recycled to the IWTP. The concentrated sludge will be pumped from the bottom of the tank to the hydrogen peroxide oxidation unit.

- c. Oxidation Unit

The oxidation unit will consist of an oxidation tank, mixer, pH control system, and hydrogen peroxide addition system. Sufficient residence time will be provided in the mix tank to allow the sulfide oxidation reactions to take place. The mix tank will be baffled to provide three stages of oxidation to minimize short circuiting. It is expected that little oxidation of the organic species in the concentrated sludge will occur; however, oxidation of the sludge will allow the hydrocarbon to form a separate liquid phase. At least one foot of freeboard will be provided with the oxidation tank to contain foaming caused by oxygen generation.

The hydrogen peroxide feed system will consist of a tank (possibly the shipping container), metering pump, and flow meter. This system will be designed in accordance with the recommended practices of the hydrogen peroxide supplier to minimize the possibility of rapid decomposition of the hydrogen peroxide due to contamination, incompatible materials, or spills. Hydrogen peroxide at 35 percent (wt) will be used (versus higher concentrations) to minimize problems associated with shipping and storage and the possibility of accidental rapid decomposition.

The pH control system will include a sodium hydroxide storage container, metering pump, and controller. The pH of the oxidation tank effluent will be adjusted during testing to determine the optimum pH for the oxidation reactions.

It is not anticipated that treatment of the oxidation tank off-gas will be required. This will be reevaluated, based on the results of initial testing.

Capability will be provided to adjust the flow of concentrated sludge to the oxidation tank and/or the hydrogen peroxide addition rate to optimize the oxidation process. Hydrogen peroxide addition will be controlled by either flow ratio control to the feed sludge flow rate or using on-line or

off-line analyses. Oxidized sludge will be pumped to the phase separation unit on level control.

d. Phase Separation Unit

The phase separation unit consists of a cone-bottom tank similar to the gravity settler provided for concentration of the feed sludge except that oil skimming capability will be provided. The oxidized sludge will separate into liquid hydrocarbon, aqueous, and metal-bearing sludge phases. The hydrocarbon will be skimmed from the surface, possibly using a three baffle system, and collected in drums for off-site disposal or on-site recycle.

The aqueous phase will be drawn from the middle of the tank and either routed to a floor drain by gravity and recycled to the IWTP or treated by a dedicated ion exchange system including pretreatment by granular media and activated carbon filtration. The need to treat this stream with a dedicated ion exchange system to remove heavy metals will be determined based upon whether or not a full-scale ion exchange system will be installed to polish the IWTP effluent.

The sludge will be pumped from the bottom of the tank to the dewatering unit.

e. Dewatering Unit

The sludge from the phase separation unit will be directed to a sludge holding tank. The sludge collected in the holding tank will be periodically pumped to a centrifuge where it will be dewatered in a batch operation. A basket-type centrifuge is a likely candidate for this service. It is expected that the dewatered sludge will contain at least 25 percent solids, by weight. The dewatered sludge solids will be discharged from the centrifuge manually and loaded into drums for shipment off-site to the pyrometallurgical unit vendor. The filtrate will be routed to a floor drain and recycled to the IWTP.

Testing of a pyrometallurgical process for metal recovery will be performed by an off-site vendor. The sludge will be treated at high temperature under reducing conditions to produce ferrochromium, which can be used in the manufacture of alloys and a nonhazardous slag.

5. Material Balance

As discussed in the previous section, the recommended pilot-plant process was simulated with the performance of each unit based on the laboratory studies conducted during the first stages of this program or on vendor data. The resulting material balance is given in Table 27. The assumptions made in generating this material balance were made primarily with the intention of determining conservative flow rate and composition values for sizing and selecting equipment and not to generate actual expected stream compositions. The stream numbers given in the material balance correspond to those shown in the process block diagram in Figure 8. Note: The letters in column 2 of the material balance correspond to separate material balances for two assumed feed solids concentrations (a. corresponds to 0.3 percent and b. corresponds to 1.0 percent solids).

6. Equipment List

Equipment size estimates were based on a ten-to-one volume reduction from 5000 gallon/day to 500 gallon/day in the initial sludge concentration unit. This decrease corresponds to the increase in concentration of the sludge experienced in laboratory tests for froth flotation. The settling tank may also be used as a holding tank, and is sized to contain the flow from an 8-hour shift. The equipment sizes listed in Table 27 (and therefore costs) may change based on further evaluation of the expected performance of the gravity settling tank. A more complete equipment list follows:

TABLE 27. MATERIAL BALANCE FOR PILOT PLANT PROCESS.

Stream Number	0	1	2	3	4	5	6	7	8	9	10	11
Mass Flow (Kg/day)												
a	18982	19443	17038	2226	1890	325	10.8	36.1	289	31	4	4
b	19116	441	15675	3914	2707	1168	39.4	129.8	1038	112	14	13
Mass Flow Influent (Kg/day)				283 478								
a												
b												
% Suspended Solids (Wgt %)	a	0.3	2.64	0.03	2.23	0.35		90	0			
b	b	1.0	5.00	0.12	4.23	0.42						
% Metal Sulfide of SS (Wgt %)	a	20	20	20	18	42		18.8	0			
b	b	20	20	20	18	42		21.4	0			
% Organic of SS (Wgt %)	a	25	25	25	26	29		0.4	0			
b	b	25	25	25	26	29		0.4				
% Inerts of SS (Wgt %)	a	55	55	55	56	29		81.8	0			
b	b	55	55	55	56	29		78.2	0			
Dissolved Ions												
Fe ($\mu\text{g/g}$)			0.395		0.20				2.20			
Cr ($\mu\text{g/g}$)			0.076		4.50				4.50			
Cd ($\mu\text{g/g}$)			0.001		0.21				0.21			
Pd ($\mu\text{g/g}$)			0.002		0.03				0.03			
Ni ($\mu\text{g/g}$)			0.016		5.10				5.10			
Other ($\mu\text{g/g}$)			0.040		6.60				6.60			
SO ₄ ($\mu\text{g/g}$)	a		0.000		3104				3104			
b	b		0.000		8879				8879			
Na ($\mu\text{g/g}$)	a		0.000		0.000				0.00			
b	b		0.000		0.000				0.00			

TANKS:

Sludge feed tank (optional)
Gravity settler
Oxidation tank
H₂O₂ container
NaOH container
Oil/water/sludge separator
Oil container
Sludge holding tank
Dewatered sludge solids container

MIXERS:

Feed tank mixer (optional)
Oxidation tank mixer

PUMPS:

SCC sludge feed pump
Feed tank sludge pump (optional)
Concentrated sludge pump
Oxidized sludge pump
H₂O₂ metering pump
NaOH metering pump
Treated sludge pump

OTHER:

Basket-type centrifuge.

7. Cost Estimate

An economic analysis of the alternatives for the pilot plant was performed as part of the overall metals recovery validation project. The results of this analysis aided in the selection of the final process. This economic analysis was based on rough order-of-magnitude costs and is only an estimate of the costs involved in purchasing and installing equipment for the pilot plant, and testing the pyrometallurgical process. Other project costs, such as engineering labor to operate the plant during the testing phase and to prepare reports, are not included in this estimate. These costs can be found in the project cost account plan. The estimated cost of the pilot plant is outlined in Table 25.

The cost of constructing a pyrometallurgical facility at Tinker AFB is not included in Table 25, but is estimated at \$1-4 million. The decision to build such a facility would depend on the plant's ability to solve other costly sludge problems for the U.S. Air Force. This option appears feasible, but would require further research.

SECTION V

CONCLUSIONS

The SCC underflow sulfide sludge is amenable to treatment for separation and recovery of heavy metals. The preferred method of treatment is to concentrate the sludge solids, oxidize the sulfides in these solids to sulfates, separate the oil and grease, an aqueous phase, and oxidize the solids. The oil and grease would be combined with similar materials from the IWTP skimming operation. The aqueous phase would be processed for separation and recovery of contained heavy metals. The oxidized solids would be dewatered then subjected to a pyrometallurgical process to make a ferrochromium alloy and a slag phase.

The preferred method for concentration of the solids from the sulfide sludge is by gravity settling. Hydrogen peroxide is the preferred treatment for oxidation of the sulfides in the sludge. A gravity separation procedure is the preferred method for separating the oil and grease, aqueous, and oxidized solid phases. A basket centrifuge is the preferred process for dewatering the oxidized sludge solids. The preferred method for treating the oxidized sludge solids is to send them to an off-site processor to make a ferrochromium alloy and slag.

Froth flotation was found to produce a concentrate that contained 90 percent of the solids and 10 percent of the water, the remaining solids and water would be recycled to the plant and eventually recovered. Similar results may be achieved by gravity separation. Froth flotation has an estimated capital cost of \$27,200 and a utilities cost of about \$90 per day; chemical cost would be about \$1 per day. Gravity separation has an estimated capital cost of \$18,500 and a near zero operating cost. From an economic point of view, gravity separation is the recommended process.

The concentrate was treated by electrooxidation, hydrogen peroxide, and wet air oxidation. The treatment oxidized the sulfides to sulfates and released the bound oil and grease. A sludge is produced that primarily contains metal oxides and hydroxides. Some low solubility sulfates, e.g., lead and barium sulfates may also be present in these solids. The oil and grease are released and float to the top of the reactor. Some metals, e.g., nickel, are solubilized and remain

in solution. The capital cost of electrooxidation is estimated to be \$25,500 with an operating cost of \$22/day for electricity, \$39/day for salt, and an annual operating and maintenance cost of \$4,700. Hydrogen peroxide oxidation has an equipment cost of \$4,450, an operating cost of \$2/day for utilities, \$324/day for chemicals, and an annual operating and maintenance cost of \$480. Wet air oxidation has a capital cost of \$2,500,000 and operating and maintenance costs that exceed alternate technologies. Hydrogen peroxide was selected as the method recommended for the pilot plant.

The engineering design calls for a gravity separator to separate the oil and grease from the aqueous and solid oxide phases. The oxide sludge would settle to the bottom of the separator where it would be removed for further treatment. The cost of the separator is estimated to be \$5,800 with a utility cost of \$0.49 per day.

The oil and grease would be collected and could be combined with similar materials from the skimming operation in the IWTP.

The aqueous phase would be treated by ion exchange to recover dissolved heavy metals. All aqueous residues would be recycled to the IWTP. The heavy metal salts would be recycled into the industrial sector.

The oxide sludge solids would be dewatered by a centrifuge. The cost of this unit is \$26,000 with a utility cost of \$10.70 per day.

The dried sludge solids would be treated by a pyrometallurgical process to produce a ferrochromium alloy and a slag. The ferrochromium would be sold for alloy preparation. The slag meets EPA's toxicity characterization leaching procedure criteria and will be formed into an insulation material. The estimated pyrometallurgical equipment cost is \$100,000. The plan is that the dewatered sludge solids will be treated off-site by an off-site processor specializing in materials of this type.

SECTION VI RECOMMENDATIONS

Two results of this program leads to two recommendations. The first recommendation is that the AFCESA make a critical evaluation of the need for the technology developed in this program. This recommendation is based on the current (1991) operating conditions at the plating plant where point source treatment of effluents has reduced the heavy metal concentration in the Industrial Waste Treatment Plant to the point where surface discharge criteria are frequently met. Further, the amount of SCC underflow sulfide sludge appears to be much smaller at this time as compared to earlier (1990) practice.

The second recommendation is that if the decision is made to proceed to a pilot plant that the technology developed in this program be used.

SECTION VII

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APPENDIX A

LABORATORY PROCEDURES FOR TREATING SULFIDE SLUDGE

APPENDIX A

LABORATORY PROCEDURES FOR TREATING SULFIDE SLUDGE

A. METHOD A: PROCEDURES FOR FROTH FLOTATION TESTS

1. Purpose

The flotation tests reported here were conducted at the laboratories of Advanced Processing Technologies, Inc., (APT) Salt Lake City, Utah. The flotation experiments were designed to test the ability of air sparged hydrocyclones (ASH), as well as conventional flotation cells, to separate solids from the sludge.

Froth flotation results in the separation of solids from a slurry. The process concentrates a portion of the solids and rejects a portion of the liquid. In the context of the present tests the purpose of froth flotation is to concentrate the solids to reduce reagent requirements in the follow-on unit processes.

2. Equipment Required

Denver Equipment Co. Model D-12, Laboratory Flotation System with a 1.0 liter cell. Equivalent systems are equally acceptable.

Syringe for addition of frother. The syringe used in the present tests delivered drops that provided a concentration of 5 milligrams per liter of methyl isobutyl carbinol in one liter of slurry per drop of frother.

Graduated cylinder, 1 liter, for measuring volume of slurry to be tested.

Pans for catching overflow. Stainless steel pans were used to collect the concentrate produced by the process. The pans are to be tared prior to use.

- Skimmer for scrapping the froth from the cell into the collecting pan.

Squirt bottle with water for washing the sides of the cell and the center column of the cell. Tap water was used in this process.

Filter paper for collecting the solids produced during the test.

Pressure filter for making liquid-solid separations.

3. Sample

The 5-gallon (19 liter) sample of sludge used in the tests reported here was collected at Tinker Air Force Base on May 11, 1991. Tests showed that the sludge used in the present study had a solids content of about 0.35 weight percent. The sample was gathered at the Solids Contact Clarifier (SCC) underflow discharge line by filling a 5-gallon carboy and then allowing the solids to settle. The supernatant was decanted and the bottle refilled with sludge. This two-stage collection procedure resulted in a slightly concentrated sludge. From the description of the sampling procedure, the underflow was estimated to contain 0.2 to 0.3 weight percent solids. The slurry had been previously reported to have a solids concentration in the range of 1 to 3 weight percent. Point source treatment of the plating wastes has resulted in significantly less heavy metal entering the Industrial Wastewater Treatment Plant (IWTP) and, consequently, a lesser quantity of solids produced at the SCC underflow.

4. Chemicals

Polymers were added to test the response of the sludge to their addition. Betz Industrial (division of Betz Laboratories, Inc.) polymers 1195, a cationic polymer, and 1125, an anionic polymer, (or their equivalents) are used to promote agglomeration and settling in the solids contact clarifier. These polymers were present in the sludge solids and were not tested in the present series of experiments. The Betz Laboratories technical representative recommended that the Betz polymers noted below be used for testing. Other

chemicals are those conventionally used or those recommended for testing by APT personnel.

Methyl isobutyl carbinol (MIBC), (4-methyl 2-pentanol), a frother used to develop a froth column in the cell. This chemical is used without prior dilution. Addition is made using a syringe that produces 5 milligrams drops, thus one drop of MIBC in the cell results in 5 milligrams per liter of MIBC in the sludge.

Potassium amyl xanthate, a collector for sulfide minerals. A 10 percent solution was prepared and used to treat the sludge.

Potassium monopersulfate, an oxidizer. This was used to perform some oxidation of the sulfides in the flotation cell. This material was added without prior dilution.

Betz 1175 polymer, added without prior dilution to achieve a concentration of 10 milligrams per liter.

Betz 1180 polymer, added without prior dilution to achieve a concentration of 10 or 25 milligrams per liter.

Betz 1190 polymer, added without prior dilution to achieve a concentration of 10 milligrams per liter.

5. Procedure for Tests 1 through 8

1. Set the speed of the cell at 1000 revolutions per minute using the adjusting knob of the variable speed drive and a tachometer mounted on the spindle. Turn the motor off.
2. Measure 1 liter of the mixed sludge into the flotation cell using the graduated cylinder. One liter of as-received sludge was used in Tests 1 through 8.

3. Turn the machine on and mix for one minute. Add flotation chemicals during this time.
4. Open the air valve and admit air into the machine. Note the time to the nearest second.
5. Skim the froth for 1 minute to make the first concentrate. Collect the concentrate in a tared pan.
6. Weigh the pan and concentrate to determine the weight of the concentrate.
7. Wash the sides of the cell and the standpipe using the wash bottle. Add additional water to bring the volume to about 1 liter.
8. Repeat Steps 4 through 6 to collect a second concentrate.
9. Shut off the air and the motor.
10. Wash the sides of the cell and the standpipe; remove the cell from the machine.
11. Filter the two concentrates and the sludge remaining in the cell.
12. Dry and weigh the residues from the concentrate and sludge remaining in the cell.

6. Procedure for Test 9

The protocol for Test 9 was significantly different from that of Tests 1 through 8.

1. Pressure filter eight liters of as-received sludge. [23.7 grams of solids (dry weight, including organics) and eight liters of filtrate were produced.]
2. Use one liter of the filtrate to disperse the solids and make one liter of slurry. (The resulting slurry was 2.37 percent solids and simulates the previously-reported nominal solids content of the sludge, i.e., 1 to 3 percent solids. The filtrate was clear, but had a light straw color at the time it was collected. Upon standing for a few minutes the solution became cloudy as a yellow-white precipitate developed, and the amount of turbidity increased with the passage of time. This precipitate was similar in appearance to elemental, colloidal sulfur produced in other systems and is believed to be elemental sulfur formed due to air oxidation of the excess sulfide in the filtrate.)
3. Measure 1 liter of the mixed sludge into the flotation cell using the graduated cylinder. (One liter of reconstituted, concentrated sludge was used in Test 9.)
4. Turn the machine on and mix for one minute. Add flotation chemicals during this time.
5. Open the air valve and admit air into the machine. Note the time to the nearest second.
6. Skim the froth to make the first concentrate. Note the time for collection. Collect the concentrate in a tared pan.
7. Weigh the pan and concentrate to determine the weight of the concentrate.

8. Wash the sides of the cell and the standpipe using the wash bottle. Add additional water to bring the volume to about 1 liter.
9. Repeat steps 4 through 6 to collect a second concentrate. Continue collecting concentrates until visual observations of the sludge indicate that most of the solids have been removed.
10. Shut off the air and the motor.
11. Wash the sides of the cell and the standpipe, remove the cell from the machine.
12. Filter all concentrates and the sludge remaining in the cell.
13. Dry and weigh the residues from the concentrate and sludge remaining in the cell.

7. Filtration of Flotation Concentrates and Residual Cell Contents

The sludge is slow to filter by gravity or by vacuum filtration. The use of a pressure filter markedly increased test productivity. The pressure filter used is one designed by ATP and sold through a distributor. The Filter consists of a barrel, a base plate, a cover, and a yoke.

1. Assemble the pressure filter. Place the filter paper on the base plate. Place an elastomer gasket on the filter paper and place the barrel on the gasket. The cover is fitted with an elastomer gasket. Place the cover on the upper end of the barrel and secure with the yoke.
2. Add the sample to be filtered to the filter press. This may be done prior to placing the cover on the barrel if the volume of sludge is small. If the volume of sludge to be filtered is

large, it is usually best to pour the sludge through the ball valve on the cover; use a funnel to reduce losses.

3. Place the cover plate in place and secure with the yoke.
 4. Admit air to the filter to a pressure of 40 to 60 pounds per square inch gauge.
 5. Collect the filtrate at a drain tube in the base plate. (The use of tared filter paper will markedly improve productivity and result in less loss of sample into the pores of the paper.)
 6. At the end of the filtration, turn the air pressure off and vent the excess pressure in the vessel through the ball valve provided on the cover.
 7. Disassemble the filter press and remove the filter paper and its load of residue. Dry the residue.
8. Drying Samples from Froth Flotation Tests

The filter and residue from each filtration were dried in an oven at about 110°C until dry. (The high surface area of the filter and residue permitted drying in about 15 minutes.)

9. Disposal of Samples and Residual Materials

The sludge may contain toxic metals in excess of those allowed for discharge without prior treatment. The subcontract from EG&G Idaho, Inc., to Advanced Processing Technologies, Inc., required that EG&G Idaho accept all samples and residual materials for disposal. (These residues were combined with other Tinker AFB materials on hand and shipped to a repository on October 25, 1991.)

1. Filter any remaining sludge.
2. Dry the residue and ship to EG&G Idaho for final disposition.
3. Add calcium hypochlorite to the filtrate to oxidize any sulfides remaining in solution. The oxidized filtrate will have metal and sulfide concentrations that meet local discharge requirements.
4. Discharge the oxidized filtrate to the sanitary sewer.

10. Calculations

1. Solids in sample, percent. Determine the total weight of solids recovered by flotation plus the weight of solids in the sludge remaining in the cell at the end of the test. As a first approximation, the volume of the water is the volume of the sludge used in the test, 1000 milliliter.

$$\frac{\text{Percent solids}}{\text{sample}} = 100 \times \frac{\sum \text{weight of solids}}{\text{weight of slurry} - \sum \text{weight of solids}}$$

2. Solids in concentrate, percent. Determine the weight of solids in the concentrate. This will usually be the weight of the dried filter paper plus the concentrate minus the weight of the filter paper. A first approximation of the weight of the sludge collected, in grams, will be the weight of water in the concentrate. Since the density of water is very nearly 1 gram/milliliter the volume of water, in milliliter, it is numerically the same as the weight of water.

$$\text{Percent solids} = 100 \times \frac{\sum \text{weight of solids in sample}}{\text{weight of slurry} - \sum \text{weight of solids}}$$

3. Solids distribution, percent. The solids in a concentrate divided by the total solids in the sample gives the solids distribution for a concentrate or the residual sludge in the cell.

$$\text{Percent solids distribution} = 100 \times \frac{\text{weight of dry concentrate}}{\sum \text{weight of dry solids}}$$

4. Water rejection, percent. The percent water collected in the concentrate is the retained water. The percent of water rejected is 100 minus the percent of water retained. The weight of water in the sample is typically about 1000 grams.

$$\frac{\text{Percent water rejected}}{\text{rejected}} = 100 - 100 \times \frac{\text{weight of sludge collected} - \text{weight of solids}}{\text{weight of sample water}}$$

B. METHOD B: CONCENTRATING AND ANALYZING TINKER SLUDGE

A 0.3 percent solids sulfide sludge from the Tinker AFB metals solids contact clarifier was filtered to near dryness. A sample of this filtered sludge was taken and oven dried to determine the percent solids after filtration. The filtered sludge was then reconstituted with a volume of the original filtrate to produce a 10 percent solids sludge for testing. Two samples at 1 gram each of the reconstituted sludge were digested with nitric acid in microwave digestion bombs and analyzed by inductively-coupled plasma atomic emission spectrophotometry (ICP-AES) to determine the metals content.

C. METHOD C: ELECTRODEPOSITION DURING ELECTROOXIDATION OF SULFIDE

Electrodeposition of metals on the cathode during electrooxidation was tested by mixing 50 grams of 10 percent solids sludge with 2 grams of sodium chloride and bringing the mixture to 100 grams with water in a stirred 250 milliliter polypropylene bottle. Two carbon electrodes were inserted through the lid and a potential of 4.0 volts was applied, producing a current flow of

1.0 amps. Within 1/2 hour the sludge had turned from black to a beige color. After 1 hour the power was shut down; the cathode was removed, rinsed with deionized water, and then stripped with 10 milliliter of concentrated nitric acid. The acid was diluted to 100 milliliter with deionized water and analyzed by ICP-AES. A sample of the oxidized solution was then filtered through a 0.2 μ m Acrodisc filter to remove additional sludge solids, acidified, and analyzed to determine soluble metals.

D. METHOD D: THERMODYNAMICS OF SLUDGE-HYDROGEN PEROXIDE REACTION

Two 100 milliliter volumes of a 1 percent solids Tinker sludge were placed in dewar flasks and allowed to equilibrate to temperatures of 21.0 \pm 0.1°C before receiving 100 milliliters of a 3 percent hydrogen peroxide solution at 19.0 \pm 0.05°C. The temperature was recorded at 0.5 minute intervals throughout the experiment. The hydrogen peroxide was added slowly over the first 10 minutes to keep the reaction mixture from frothing over the dewar walls.

E. METHOD E: HYDROGEN PEROXIDE TREATMENT OF SULFIDE SLUDGE

Tinker sludge was exposed to varying concentrations of hydrogen peroxide and the resultant solutions were analyzed for soluble metal versus time. Ten percent solids sludge samples of 25.0 \pm 0.5 gram of were mixed with 25.0 \pm 0.5 gram of 2, 4, or 8 percent hydrogen peroxide for 10, 20, 40, and 80 minutes. The resultant solutions were then centrifuged to pellet and the solids removed from bulk solution after each specified reaction time. Samples of the supernatant were then passed through a 0.2 μ m Acrodisc, acidified, and analyzed for metals to determine the soluble metal vs. time of reaction.

F. METHOD F: FILTRATION TESTS FOR OXIDIZED SLUDGE

Four filtration tests were made. Two tests were made using SCC underflow sludge without pretreatment. Two tests were made using SCC underflow sludge that had been oxidized using hydrogen peroxide.

1. - Untreated SCC underflow sludge

The treatment was performed by measuring 200 milliliters of well-stirred SCC underflow sludge into a graduated cylinder. The sludge was then transferred to a 500 milliliter Erlenmeyer flask. Water, 200 milliliters, was added to the sludge to bring the volume to 400 milliliters.

2. Oxidized SCC underflow sludge

The treatment was performed by measuring 200 milliliters of well-stirred SCC underflow sludge into a graduated cylinder. The sludge was then transferred to a 500 milliliter Erlenmeyer flask. Hydrogen peroxide, 3 percent, solution was added over a period of 30 minutes at an average rate of 6 to 7 milliliters per minute for a total volume of 200 milliliters. The flask was mixed continuously during the addition of the peroxide. After the hydrogen peroxide addition, the flask was allowed to stand for 2.5 hours before filtering.

3. Filtration Procedure

The filtration was performed with a Fisher Model 09-753-25J pressure filtration apparatus at 5 psi with a predried (2 hours at 105°C) Fisher #5 fine filter paper. The filter was preweighed before placement into the filter apparatus. The sludge slurry was poured into the top of the apparatus via a plastic funnel. The sludge flask and the funnel were then rinsed with 100 milliliters of water to make the sludge transfer to the filter apparatus more quantitative (total filtered volume becomes 500 milliliters). The cap was then placed on the apparatus and the pressure then applied at 5 psi. The volume of filtrate in milliliters was recorded versus time in seconds.

G. METHOD G: SEDIMENTATION TEST

Four sedimentation tests were conducted: two tests were made on untreated SCC underflow sludge and two tests were made on oxidized SCC underflow sludge.

The procedures for conducting the sedimentation tests are provided in this method.

1. Method for Untreated Sludge

1. Prepare the bulk sample of the sludge by mixing it well.
2. Measure 100 milliliters of the well-stirred sludge into a 250 milliliter graduated cylinder.
3. Add 100 milliliters of deionized water to the sludge in the graduated cylinder and mix well.
4. Stop mixing and observe the interface between the more-or-less clear liquid phase and the top of the settling solids. Measure and record the distance settled, from the bottom of the graduated cylinder, as a function of time.
5. Note any anomalies, such as a large amount of floating solids.
6. Make a graph of the distance settled as a function of time. This is referred to as a Kynch curve.

2. Method for Sedimentation Tests on Oxidized SCC Underflow Sludge

1. Prepare the bulk sample of the sludge by mixing it well.
2. Measure 100 milliliters of the well-stirred sludge into a beaker.
3. Add 100 milliliters of 3 percent hydrogen peroxide to the sludge in the beaker slowly enough to avoid excessive frothing and loss of sample from the beaker.

4. Allow the reaction to continue, with mixing, for at least 2 hours or until no further gas evolution is observed.
5. Transfer the well-mixed, oxidized sludge, from step 4 to a 250 milliliters graduated cylinder.
6. Stop mixing and observe the interface between the more-or-less clear liquid phase and the top of the settling solids. Measure and record the distance settled, from the bottom of the graduated cylinder, as a function of time.
7. Note any anomalies, such as a large amount of floating solids.
8. Plot the distance settled as a function of time on this Kynch curve.

Note: Measure the inside dimensions of the graduated cylinder. For convenience in making the measurements, a correlation between the volumetric graduation on the cylinder and their distance from the inside bottom of the cylinder is frequently helpful. The inside diameter of the graduated cylinder was 1.44 inches. The correlation between the graduations and distance from the bottom of the cylinder is given below.

Calibration of 250 milliliter graduated cylinder

Indicated Volume	Height From Bottom
0 milliliters	0 inches \pm 0.02 inches
10	0.40
30	1.14
50	1.88
70	2.62
90	3.36
110	4.10
130	4.84
150	4.58

Calibration of 250 milliliter graduated cylinder

Indicated Volume	Height From Bottom
170	6.32
190	7.06
210	7.80
230	8.54
250	9.26

H. METHOD H: ELECTROOXIDATION OF SULFIDE SLUDGE

1. Carbon electrodes

Fifty grams of 10 percent solids sludge was mixed with 2 grams of sodium chloride and brought to 100 grams with water in a 250 milliliter polypropylene bottle with two carbon electrodes inserted through the lid. A potential of 4.0 volts was applied resulting in a current flow of 1.0 A. After 1/2 hour the sludge had turned from black to beige. After 1 hour there was no visual evidence that the reaction was continuing and the power was shut down. The cathode was then immediately rinsed clean with 10 milliliters of concentrated nitric acid. The acid was diluted to 100 milliliters with deionized water and analyzed by ICP-AES. The oxidized solution was then filtered, acidified, and analyzed to determine soluble metals.

2. Platinum electrodes

Sulfide destruction was tested by placing 2 grams of dry sludge and 2 grams of sodium chloride into a 250 milliliter polypropylene bottle and brought to 200 grams with deionized water. An 8 centimeters² cathode and an 8 centimeters² anode, both platinum, were mounted to the cap and were spaced 1 centimeter apart. A potential of 2 volts was applied and a current of 0.20 A resulted and remained constant for the 2 hour duration of the experiment. Samples were drawn during the experiment and later analyzed for free sulfate.

I. METHOD I: SODIUM HYPOCHLORITE TREATMENT OF SULFIDE SLUDGE

Approximately 25 milliliters of SCC underflow sludge was contacted with about 25 milliliters of commercial bleach having a sodium hypochlorite concentration of about 5.5 percent in a stoppered test tube. The test tube was mixed by inverting at a rate of about 120 inversions per minute. Visual observations were made over 2 hours, then the mixing was terminated because of lack of visual change in the sludge solids. The samples were allowed to stand for an additional 22 hours with occasional visual observations made.

J. METHOD J: METAL ELECTRODIALYSIS DURING ELECTROOXIDATION

The method involves placing a known quantity of sludge into the central anodic chamber of a three-chambered electrochemical cell. The left (cathode) chamber receives 150 milliliters of water and or water containing catholyte solids, which contain sodium carbonate and sodium sulfate. The central sludge-containing chamber receives 3 grams of sodium chloride and is brought to 150 milliliter with water. The right and most anodic chamber receives 150 milliliters of water. The right and left chambers receive an 8 centimeters² platinum electrode each. The central chamber receives 2-2 centimeters² platinum electrodes. Between the left and central chambers is placed a 2 inch diameter cationic membrane. Between the central and right chambers is placed a 2 inch diameter anionic membrane. A potential is applied at 12 to 32 Vdc with a combination of the anodic voltages summing to the opposite of the cathodic voltage. The current and progress of metals separation, metals deposition, and sulfide oxidation is monitored during the course of the applied voltage.

K. METHOD K: PROCEDURE FOR SODIUM BOROHYDRIDE TREATMENT OF TINKER AFB SOLUTIONS

Equipment

Reagents

Various beakers, to 500 milliliters	10.0 percent H_2SO_4 solution
Various pipettes, 2.0 milliliters	10.0 percent NaOH solution
Burette, 25 milliliters	10.0 percent VenMet™ solution

Volumetric flasks	5.0 percent NaHSO_3 solution
Short range pH paper (4-9)	1.0 percent $\text{Al}_2(\text{SO}_4)_3$ solution
ORP meter (Ag/AgCl reference)	0.10 percent Betz 1120 solution
Magnetic stir plate, stir bars	

1. In a 100 milliliter volume flask, add 50 milliliters DI H_2O , 1.2 gram of SBH, 4.0 grams of NaOH, and dilute to volume with DI H_2O . This solution is equivalent to the VenMet™ diluted 10:1, is stable, and may be stored if desired.
2. Make up 10 milliliters of a 5 percent solution of sodium bisulfite (SBS, NaHSO_3) in a volume flask. Adjust the pH to 6.0 - 7.0 with NaOH to prevent SO_2 evolution. Less than 10 milliliters will be needed for this experiment, so 0.5 grams of SBS in 10 milliliters of DI water should be adequate. This solution is not stable, should not be capped, and should be neutralized and discarded after 6-8 hours. The SBS is used to destroy residual oxidants in solution prior to introduction of SBH as well as to prevent metals precipitated by SBH from reentering solution. It is much cheaper than SBH and is used to reduce SBH consumption.
3. Make up a 1 percent solution of Al sulfate. To 0.97 grams of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (to yield 0.5 gram $\text{Al}_2(\text{SO}_4)_3$) add 50 milliliters of DI water in a volume flask. This solution is stable and may be stored.
4. Make up 20 milliliters of a 0.1 percent solution of an anionic polymer (Betz 1120) by adding 20 milliliters DI water to 0.02 (20 milligrams) of polymer in a volume flask.
5. Obtain the 400 milliliters of solution recovered from the H_2O_2 treatment. This solution is obtained from Step 7 of the H_2O_2 treatment of the sulfide sludge by washing the residue with DI water and collecting the filtrate in a graduated cylinder. If the recovery and separation processes were 100 percent efficient this

solution should contain 0.142 grams (\approx 350 parts per million) each of Ag, Cd, Cu, Mn, Ni, Sn, and Zn, and 0.012 grams (\approx 30 parts per million) of Pb.

6. Add clean stir bar, determine pH, and adjust pH to 4.0 to 5.0.
7. Add Al sulfate solution to achieve 200 parts per million in the 400 milliliters (8.0 milliliters of 1 percent solution) while stirring.
8. Using graduated cylinders, divide 400 milliliters solution containing metal ions into four equal parts. Use 250 milliliter beakers and have a stir bar in each.
9. Add SBS solution to each vessel to obtain 200, 400, 600, and 1000 parts per million. This will require 0.4, 0.6, 1.2, and 2.0 milliliters, respectively, of the 5 percent SBS solution. Stir each for 10 minutes.
10. Set up oxidation-reduction potential (ORP) meter. (Also, verify type of reference cell in this instrument.)
11. Load burette with 20 milliliters of 10 percent SBH solution. Beginning with the beaker containing 200 parts per million SBS, slowly (10 to 15 drops/minute) add SBH solution to beaker while stirring. The burette tip should be near the surface and may be immersed once the flow rate has been established. The end point, as measured by the ORP meter, is -600 to -650 millivolt (Ag/AgCl reference). The pH will be monitored periodically during the run as it increases with added SBH solution. The pH should not rise above 6.5. The original ORP should be between +200 and -100 millivolt. As addition of SBH proceeds, the solution will become black and the ORP will range between -300 and -500 millivolt. Record the milliliter of SBH required to obtain an ORP reading of between -600 and -650 millivolt. Stirring time after reaching the end point should be at least 15 minutes.

12. Allow the precipitate to settle for at least 1/2 hour.
13. Add 5 parts per million polymer to each vessel (0.5 milliliters of 0.1 percent solution) and stir slowly for 3 to 5 minutes.
14. Allow solids to settle for at least 1/2 hour. Note differences, if any are apparent, in the settling characteristics.
15. Filter and save residue. Since this experiment is intended to determine how much SBS is required to enable the minimum SHB addition, the contents of the four beakers may be passed through the same filter and the remaining solution placed in the hazardous waste discard container. The residue may be fused into a bead with a torch or bunsen burner and saved for later examination if desired.
16. Repeat Steps 5 through 14 with the following exceptions:
 - (a) Wash through the filter after the H_2O_2 treatment (Step 7) to produce 100 milliliter of solution containing 0.142 grams (≈ 1400 parts per million) of the ions listed plus 0.003 grams (≈ 30 parts per million) Pb.
 - (b) Do not divide the solution as in Step 8.
 - (c) Add four times the amount of 5 percent SBS solution that was determined to be optimum in Step 9.
17. Filter. Wash residue with 25 milliliters of DI water. Send sample of residue and filtrate for analysis. Dispose of balance of solution in hazardous waste discard container. Dry residue, fuse into a bead as in Step 15 and submit for EDS analysis.
18. Repeat Steps 16 and 17 for samples of synthetic sludge with organics and for Tinker AFB sludge.

L. METHOD L: PROCEDURES FOR ION EXCHANGE TESTS FOR TINKER AFB SULFIDE SLUDGES

This procedure is to implement the ISRG-approved (MNM-21-91) experiment "Ion Exchange Tests for Tinker Air Force Base Sulfide Sludge," RLM-32-90, and consists of the detailed procedure necessary to conduct this experiment.

The first part of this effort should be considered as a screening test to determine the relative effectiveness of four candidate ion exchange resins for removing metals from the waste stream that results from treating the sulfide sludge with hydrogen peroxide. This test series will evaluate the cation exchange capacity (CEC) of the four resins and will be divided into four parts: (1) calibration of the resins to establish actual resin capacities, (2) generation of a solution of a composition expected to result from treating synthetic sulfide sludge with H_2O_2 , (3) exposing the calibrated resins to this solution at 3 pH levels, using quantities of resins that are more than adequate to remove all the ions of interest, and (4) exposing the four resins as in (3), but in quantities insufficient to remove all the ions of interest.

The data obtained from this work should enable selection of a resin (possibly two resins) that appear as most suitable for treating Tinker AFB sludge. The resin or resins and conditions that produce the best results in the simulated solution will be used to treat the product of the H_2O_2 treatment (described in another procedure) of both synthetic and Tinker AFB sludges to further evaluate its performance. If the performance is satisfactory, experiments will be set up with the resin in a column to establish procedures for regeneration of the resin and treatment of the eluant. This will enable procedure demonstration on a bench-scale pilot setup.

1. It will be necessary to "calibrate" the candidate resins to determine their total exchange capacity prior to conducting the experimental work. The resins will be the cation type: DP-1, IR-120 Plus, IRC-718, and CSA MS5. Resin calibration is done using ASTM procedure D2187-74, Methods A, B, E, and F. The data resulting from applying these methods will be used as the basis for

determining the quantity of each resin needed to strip the metal ions from the test solutions.

2. A solution simulating what would be expected to result from treating 10 grams of the synthetic sulfide sludge with H_2O_2 will be used. This solution would be diluted to 1 liter, and the composition assumes 100 percent recovery of the ions of interest, with no carryover of Cr^{+3} , Fe^{+2} , or Al^{+3} , but some carryover of Ca^{+2} and K^{+} . When 10 grams of the synthetic sludge is dissolved and diluted to 1 L, each of the ions of interest will be present at 142 milligrams per liter

SOLUTION TO SIMULATE H_2O_2 PRODUCT
(to make up 2.5 L of solution, 142 parts per million each ion)

Ion	mEquiv in 2.5 liters	Addition to 2.5 liters (grams)	mEquiv in 100 milliliters
Ag^{+}	3.29	0.513 Ag_2SO_4	0.132
Cd^{++}	6.32	0.810 $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	0.253
Cu^{++}	11.180	1.395 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.447
Mn^{++}	12.93	1.093 $\text{MnSO}_4 \cdot \text{H}_2\text{O}$	0.517
Ni^{++}	12.10	1.590 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	0.484
Pb^{++}	3.43	0.520 PbSO_4	0.137
Sn^{++}	5.98	0.450 SnCl_2	0.239
Zn^{++}	10.86	1.562 $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.435
Ca^{++}	17.72	1.526 $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}^{(a)}$	0.709
K^{+}	<u>9.08</u>	0.791 $\text{K}_2\text{SO}_4^{(b)}$	<u>0.363</u>
TOTAL	92.89		3.716

a. Can subst. 0.983 gram CaCl_2 .

b. Can subst. 0.677 gram KCl .

(142 parts per million). This value was converted to milliequivalents to enable matching resin capacity. Ca and K were added arbitrarily at 142 parts per million. Solutions used for later phases of this work will be more concentrated. The simulated solution will be made up according to the table below.

Since this is a "rich" solution, some of the ions that would be in solution in the wastewater, such as Ca, Pb, and Ag, will now appear as precipitates. When withdrawing samples for the resin tests, be sure that the solution reservoir is stirred vigorously so that the withdrawn samples contain a representative portion of the sediment.

- (3) This test will examine the behavior of the four cation resins in solutions of the ions listed above with the pH adjusted at three levels (twelve test solutions, four at each pH level, will be required). Resins will be added to the solutions in quantities sufficient to remove all the ions initially present, with some capacity to spare. Na^+ would normally be present in the solution as a carryover ion; however, sufficient Na^+ will enter the solution as a result of being dislodged from the resin by the ions of interest and the Na^+ concentration produced in this manner should equal the equivalent of ions removed from solution. Three concentrations of competing H^+ will be present by virtue of the 3 pH levels. The resin cation exchange capacities (CECs) determined by the resin calibration procedure give values for both "salt-splitting" capacity and "total" capacity. The value for salt-splitting capacity will be used for acid solutions and total capacity will be used in neutral to basic solutions. The most successful resin will be the one removing the most heavy metal ions.

Obtain a 1-liter bottle and label for storage/disposal of spent resins.

- a. Using graduated cylinders, measure 100 milliliters of the dummy solution and place into clean beakers containing cleaned stirring bars. Adjust the pH in three of the beakers to 4 (3.8-4.2) Note: Use pH 5 (4.8-5.2) for DP-1 resin, 7 (6.8-7.2), and 9 (8.8-9.2), using H_2SO_4 or NaOH, as appropriate. Record the pH actually obtained in each beaker.
- b. Each 100 milliliter beaker will contain $92.89 \div 25 = 3.716$ meq. of ions. Based on the results obtained from the resin calibration, measure sufficient resin to completely exchange all ions in solution, times a factor, as follows:

<u>Resin</u>	<u>Factor</u>		<u>Meg/dry gram</u>	<u>Gram required</u>
DP-1	3.72 x 1.25	÷	{ Slt splt 0.2655	17.495
			{ Total 7.8778	0.590
IR-120+	3.72 x 2.5	÷	{ Slt Splt 4.5359	2.048
			{ Total 4.5161	2.057
IRC-718	3.72 x 1.25	÷	{ Slt Splt 0.3529	13.162
			{ Total 6.6974	0.694
CSA MS5	3.72 x 1.25	÷	{ Slt Splt 0.7406	6.272
			{ Total 7.1279	0.652

- c. Place measured quantities of resins in beakers so that a sample of each of the four resins is exposed to the three levels of pH. Stir each beaker for at least 4 hours. The measured quantities of dry resin to be placed in each beaker are as follows:

<u>Resin</u>	<u>Nominal pH</u>	<u>Gram of dry resin</u>
DP-1	5	17.495
DP-1	7	0.590
DP-1	9	0.590
IR-120+	4	2.048
IR-120+	7	2.057
IR-120+	9	2.057
IRC-718	4	13.162
IRC-718	7	0.694
IRC-718	9	0.694
CSA MS5	4	6.272
CSA MS5	7	0.652
CSA MS5	9	0.652

- d. Measure the pH at the end of mixing. Remove the stirring bar, pour the solution through a filter into a 1.0 liter volume flask to remove the resin and remaining sediment. Use NP water to wash the resin and sediment and to dilute the solution to 1 liter. Repeat for each of the above tests. Remove sample from the 1 liter of solution for ICP analysis. When the solution analyses are completed satisfactorily, discard any remaining standard solution and the depleted solutions in the hazardous waste vessel. Dispose of resins in the resin waste bottle.
- (4) This step will be done in the same manner as Step (3), except that the quantity of resin added to each beaker will be insufficient to remove all the heavy metal cations. If resins are added at 70 percent of the amount required to remove all the added ions, this

in effect would leave no sites available for removing Ca^{+2} and K^+ . If resins are added to 60 percent of the amount needed, sites will be unavailable for Zn^{++} and/or Mn^{++} . Since Ca^{++} and K^+ supposedly have a small affinity for these resins, use the 60 percent value.

When the resins are first placed into the solutions, all of the heavy metal ions are expected to replace Na^+ . Thereafter, heavy metal ions with greater affinity for the exchange sites will displace back into the solutions those with lesser affinity. When the resins reach equilibrium with the solutions, some ions may be totally removed while others may be present in nearly their original

concentrations. This experiment will provide a figure for resin selectivity. Again, the Na^+ introduced into solution should equal the equivalents of ions removed from solution .

- a. Perform this experiment in the same manner as in Step (3), except that the quantity of resin to be added to each 100 milliliters of solution will be 60 percent of the amount required to exchange all of the ions. Each CEC value is divided into the factor to obtain the grams of dry resin, as follows:

<u>Resin</u>	<u>Factor</u>		<u>Meg/dry gram</u>	<u>Gram required</u>
DP-1	3.72 x 0.60	÷	{ Slt splt 0.2655	8.398
			{ Total 7.8778	0.283
IR-120+	3.72 x 0.60	÷	{ Slt Splt 4.5359	0.492
			{ Total 4.5161	0.494
IRC-718	3.72 x 0.60	÷	{ Slt Splt 0.3529	6.318
			{ Total 6.6974	0.333

<u>Resin</u>	<u>Factor</u>		<u>Meg/dry gram</u>	<u>Gram required</u>
			Slt Splt 0.7406	3.011
CSA MS5	3.72 x 0.60	÷	Total 7.1279	0.313

The measured quantities of dry resin to be placed in each beaker for this test are as follows:

<u>Resin</u>	<u>Nominal pH</u>	<u>Gram of dry resin</u>
DP-1	5	8.398
DP-1	7	0.283
DP-1	9	0.283
IR-120+	4	0.492
IR-120+	7	0.494
IR-120+	9	0.494
IRC-718	4	6.318
IRC-718	7	0.333
IRC-718	9	0.333
CSA MS5	4	3.011
CSA MS5	7	0.313
CSA MS5	9	0.313

b. Follow the procedure as described in Steps (3) c and d.

Depending on the outcome of this work, additional tests may be run using the scheme described above, but with pH levels higher than 4 or lower than 9.

M. METHOD M: PROCEDURE FOR TREATING SOLUTIONS WITH SODIUM BOROHYDRIDE TO
 REMOVE METAL IONS

If the SBH treatment is applied to the solution resulting from treating the 10 gram synthetic sludge sample with H_2O_2 , 0.142 grams of each of the metals will be in the solution that is separated from the hydroxides, assuming 100 percent recovery efficiency. An exception will be $PbSO_4$, most of which should remain with the hydroxides, due to its relative insolubility. Assuming no Cr, Fe, and Al carryover, Ag, Cd, Cu, Mn, Ni, Pb, Sn, and Zn ions will be in the solution to be treated. It seems unlikely that SBH will be effective in removing Mn and Zn from solution.

The general equation for the reduction of metals with SBH is:



Note that 1 equivalent of SBH will reduce 8 equivalents of metal ion.

Morton Thiokol markets an SBH solution for removal of heavy metal ions from wastewater. VenMet™ is 12 percent SBH, 40 percent NaOH, balance H_2O , and is normally diluted 10:1 before application to wastewater. A similar solution can be made up in the laboratory, since only small quantities will be needed at this stage of the work.

<u>Equipment</u>	<u>Reagents</u>
Various beakers, to 500 milliliters	10.0 percent H_2SO_4 solution
Various pipettes, 2.0 milliliters	10.0 percent NaOH solution
Burette, 25 milliliters	10.0 percent VenMet™ solution
Volumetric flasks	5.0 percent NaHSO_3 solution
Short range pH paper (4-9)	1.0 percent $\text{Al}_2(\text{SO}_4)_3$ solution
ORP meter (Ag/AgCl reference)	0.10 percent Betz 1120 solution
Magnetic stir plate, stir bars	

Note: Steps 2, 11, and 15 have potential for generating gas or fumes and should be performed in a fume hood or under an exhauster.

1. In a 100 milliliter volume flask, add 50 milliliters DI H_2O , 1.2 grams of SBH, 4.0 gram of NaOH, and dilute to volume with DI H_2O . This solution is equivalent to the VenMet™ diluted 10:1, is stable, and may be stored if desired.
2. Make up 10 milliliters of a 5 percent solution of sodium bisulfite (SBS, NaHSO_3) in a volume flask. Adjust the pH to 6.0 - 7.0 with NaOH to prevent SO_2 evolution. Less than 10 milliliters will be needed for this experiment, so 0.5 grams of SBS in 10 milliliters of DI water should be adequate. This solution is not stable, should not be capped, and should be neutralized and discarded after 6-8 hours. The SBS is used to destroy residual oxidants in solution prior to introduction of SBH as well as to prevent metals precipitated by SBH from re-entering solution. It is much cheaper than SBH and is used to reduce SBH consumption.
3. Make up a 1 percent solution of Al sulfate. To 0.97 grams of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (to yield 0.5 grams $\text{Al}_2(\text{SO}_4)_3$) add 50 milliliters of DI water in a volume flask. This solution is stable and may be stored.

4. Make up 20 milliliters of a 0.1 percent solution of an anionic polymer (Betz 1120) by adding 20 milliliters DI water to 0.02 (20 mg) of polymer in a volume flask.
5. Obtain the 400 milliliters of solution recovered from the H_2O_2 treatment. This solution is obtained from Step 7 of the H_2O_2 treatment of the sulfide sludge by washing the residue with DI water and collecting the filtrate in a graduated cylinder. If the recovery and separation processes were 100 percent efficient, this solution should contain 0.142 grams (\approx 350 parts per million) each of Ag, Cd, Cu, Mn, Ni, Sn, and Zn, and 0.012 gram (\approx 30 parts per million) of Pb.
6. Add clean stir bar, determine pH, and adjust pH to 4.0 to 5.0.
7. Add Al sulfate solution to achieve 200 parts per million in the 400 milliliters (8.0 milliliters of 1 percent solution) while stirring.
8. Using graduated cylinders, divide 400 milliliters solution containing metal ions into four equal parts. Use 250 milliliter beakers and have a stir bar in each.
9. Add SBS solution to each vessel to obtain 200, 400, 600, and 1000 parts per million.

This will require 0.4, 0.6, 1.2, and 2.0 milliliters, respectively, of the 5 percent SBS solution. Stir each for 10 minutes.

10. Set up (including calibration, figures below are based on use of Ag/AgCl reference electrode) oxidation-reduction potential (ORP) meter. (Also, verify type of reference cell in this instrument.)
11. Load burette with 20 milliliters of 10 percent SBH solution. Beginning with the beaker containing 200 parts per million SBS,

- slowly (10 to 15 drops/minute) add SBH solution to beaker while stirring. The burette tip should be near the surface and may be immersed once the flow rate has been established. The end point, as measured by the ORP meter is -600 to -650 millivolt (Ag/AgCl reference). The pH will be monitored periodically during the run as it increases with added SBH solution. The pH should not rise above 6.5. The original ORP should be between +200 and -100 millivolt. As addition of SBH proceeds, the solution will become black and the ORP will range between -300 and -500 millivolt. Record the milliliter of SBH required to obtain an ORP reading of between -600 and -650 millivolt. Stirring time after reaching the end point should be at least 15 minutes.
12. Allow the precipitate to settle for at least 1/2 hour.
 13. Add 5 parts per million polymer to each vessel (0.5 milliliters of 0.1 percent solution) and stir slowly for 3 to 5 minutes.
 14. Allow to settle for at least 1/2 hour. Note differences, if any are apparent, in the settling characteristics.
 15. Filter and save residue. Since this experiment is intended to determine how much SBS is required to enable the minimum SHB addition, the contents of the four beakers may be passed through the same filter and the remaining solution placed in the hazardous waste discard container. The residue may be fused into a bead with a torch or bunsen burner and saved for later examination if desired.
 16. Repeat Steps 5 through 14 with the following exceptions:
 - (a) Wash through the filter after the H_2O_2 treatment (Step 7) to produce 100 milliliter of solution containing 0.142 grams (\approx 1400 parts per million) of the ions listed plus 0.003 grams (\approx 30 parts per million) Pb.

.(b) Do not divide the solution divided as in Step 8.

(c) Add four times the amount of 5 percent SBS solution that was determined to be optimum in Step 9.

17. Filter. Wash residue with 25 milliliters of DI water. Send sample of residue and filtrate for analysis. Dispose of balance of solution in hazardous waste discard container. Dry residue, fuse into a bead as in Step 15, and submit for EDS analysis.
18. Repeat Steps 16 and 17 for samples of synthetic sludge with organics and for Tinker AFB sludge.

N. METHOD N: PROCEDURE FOR TREATING SLUDGE WITH HYDROGEN PEROXIDE
(supplementary procedure)

1. Weigh out 10 grams of dried synthetic or Tinker AFB sludge and place in a cleaned 100 milliliter beaker with a stirring bar. Add 15 milliliters of DI water so that the sludge resembles that which has been dewatered to 40 percent solids.
2. Adjust pH to 4.0 to 10.0 (to be specified) using H_2SO_4 or NaOH solution. Ph is a major variable for this work.
3. Dilute 30 percent or (35 percent) H_2O_2 by measuring 300 milliliters (250 milliliters) of this solution and diluting to 1 liter with DI water. Care should be taken to avoid contaminating the H_2O_2 in the original container and to preclean glassware and stirring bar with 10 percent HNO_3 solution to remove contaminants that would cause premature decomposition of H_2O_2 .
4. The diluted solution contains 0.1 grams H_2O_2 per milliliter.
5. Titrate the H_2O_2 into the sludge sample solution while stirring, recording the milliliter used. The endpoint, if obvious visually,

is not known, but the milliliter required may be estimated by determining the amount of H_2O_2 required to oxidize the amount of sulfide (and organics when present) in the sludge sample.

6. When the reactions have gone to completion, the sulfides will have been oxidized to sulfates and remobilized, and some of the organics should be oxidized to CO_2 and H_2O . The hydroxides of Fe, Cr, and Al should remain behind as sediment if the pH is higher than 7.0. Allow the beaker of solution to stand undisturbed for several hours to ensure the H_2O_2 is decomposed and the sediment is settled.
7. Filter the slurry and collect the filtrate in a 500 milliliter graduated cylinder. Wash the residue with enough DI water to produce the volume required for the next experiment and collect this wash water in the graduated cylinder. Record the total volume of this solution. Extract a sample of the filtrate for analysis and pour the solution into a clean, labeled, capped container for use in later experiments.
8. Dry the filtrate, obtain a weight, and place the dried filtrate into a sample bottle after removing about 1 gram for analysis. Discard the filter paper in the hazardous waste container.

APPENDIX B

PROCESS EQUIPMENT AND ECONOMIC EVALUATION

APPENDIX B
PROCESS EQUIPMENT AND ECONOMIC EVALUATION

Equipment size estimates were based on a decrease in flow rate from 5000 gallon/day to 500 gallon/day in the initial sludge concentration unit. This decrease corresponds to the increase in concentration of the sludge experienced in laboratory tests of froth flotation.

The settling tank is also to be used as a holding tank, and is sized to contain the flow from an 8-hour shift. Equipment sizes (and therefore costs) are likely to change based on further evaluation.

ESTIMATED PRIMARY EQUIPMENT SIZES

Equipment	Estimated Size
Settling tank	2000 gallon
Hydrogen peroxide oxidation unit	25 gallon
Oil/water/sludge separation unit	25 gallon
Centrifuge (basket-type)	20 gallon pan

SLUDGE CONCENTRATION UNIT

Froth Flootation Unit

Major Equipment	Auxiliary Equipment	Equipment Size/Type	Cost Estimate
Feed Tank	Tank w/ Stand	1000 gallon	\$ 3200
	Frother Feed Pump	Variable Speed, Metering	\$ 500
	Mixer	1000 gallon Tank Mixer	\$ 1500
	Level Detector	Float Switch w/ Electronics	\$ 500
	Feed Pump	Centrifugal	\$ 1000
	Sampler	Composite Sampler	\$ 600
	Flow Meter	Paddle Wheel w/ Electronics and Fittings	\$ 900
Flotation Unit	Flotation Cells	4 - 1 cubic foot volume	\$17,900
	Samplers	2 In-Line Samplers	\$ 200
	Flow Meter	Paddle Wheel w/ Electronics and Fittings	\$ 900
Total Estimated Cost			\$27,200

Centrifuge Unit

Equipment	Equipment Size/Type	Cost Estimate
Feed Tank w/ Stand	1000 gallon	\$ 3,200
Feed Pump	Approx. 20 gallon/hour	\$ 1,000
Centrifuge	Continuous Flow	\$45,000
Samplers	2 In-Line Samplers	\$ 200
	1 Composite Sampler	\$ 600
Flow Meters	1 Paddle Wheel Flow Meter w/ Electronics and Fittings	\$ 900
	1 Turbine Flow Meter w/ Electronics and Fittings	\$ 900
Total Estimated Cost		\$51,800

Settling Unit

Equipment	Equipment Size/Type	Cost Estimate
Tanks w/ Stands	3 - 1000 gallon tanks	\$16,000
Samplers	Composite Samplers	\$ 600
	In-line	\$ 100
Flow Meters	Paddle Wheel Flow Meter w/ Electronics and Fittings	\$ 900
	Turbine Flow Meter w/ Electronics and Fittings	\$ 900
Total Estimated Cost		\$18,500

OXIDATION UNIT

Electrolytic Oxidation Unit

Primary Equipment	Auxiliary Equipment	Equipment Size/Type	Cost Estimate
NaCl Addition Tank	NaCl Make-up Drum	55 gallon	\$ 50
	Metering Pump	Variable Speed	\$ 500
	Small Mixer	Portable Drum Mixer	\$ 200
	Addition Tank w/ Stand	500 gallon	\$ 1,450
	Feed Pump	Approx. 20 gallon/hour	\$ 1,000
	Large Mixer	500 gallon Tank Mixer	\$ 500
	Sampler	In-Line Sampler	\$ 100
	Level Detector	Float Switch w/ Electronics	\$ 500
	Flow Meter	Paddle Wheel w/ Electronics and Fittings	\$ 900
	Temperature Indicator	Thermocouple	\$ 350
Electrolytic Oxidation Cell	Cell Block	Acrylic Cell Walls, RuO ₂ Anode, Ti Cathode	\$14,000
	Feed Pump	Approx. 20 gallon/hour	\$ 1,000
	Rectifier	Approx. 250 Amperes	\$ 3,000
	Temperature Indicator	Thermocouple	\$ 350
	Sampler	In-Line Sampler	\$ 100
Off-gas System	Hood	Cl ₂ Resistant Sheet Metal	-
	Blower	To Be Determined	-
	Gas Monitor	Cl ₂	\$ 1,500
Total Estimated Cost			\$25,500

Hydrogen Peroxide (H₂O₂) Unit

Primary Equipment	Auxiliary Equipment	Equipment Size/Type	Cost Estimate
H ₂ O ₂ Solution Tank	Metering Pump	Variable Speed	\$ 500
H ₂ O ₂ Solution Addition Tank	Mixing Tank w/ Stand	100 gallon	\$ 600
	Feed Pump	Approx. 20 gallon/hour	\$ 1,000
	Tank Mixer	100 Tank Mixer	\$ 500
	Level Detector	Float Switch w/ Electronics	\$ 500
	Sampler	In-Line Sampler	\$ 100
	Temperature Indicator	Thermocouple	\$ 350
	Flow Meter	Paddle Wheel w/ Electronics and Fittings	\$ 900
Total Estimated Cost			\$ 4,450

Wet-Air Oxidation Unit

Major Equipment		Cost Estimate
Oxidation Unit	High Pressure Reactor Vessel	\$ 2,500,000
	Heat Exchanger	
	Air Compressor	
	Separation Vessel	
Total Estimated Cost		\$ 2,500,000

OIL/WATER/SLUDGE SEPARATION UNIT

Equipment	Equipment Size/Type	Cost Estimate
Tank w/ Stand	100 gallon, Conical Bottom	\$ 600
Sludge Feed Pump	Diaphragm Pump	\$ 300
Air Compressor	To run diaphragm pump	\$ 300
Level Indicator	W/ Electronics--Will measure oil/water/sludge interfaces	\$2,200
Oil Collection Drum	55 gallon	\$ 50
Oil Pump	Centrifugal	\$ 200
Level Detector	Drum	\$ 50
Flow Meters	1 - Paddle Wheel w/ Electronics and Fittings	\$ 900
	1 - Turbine w/ Electronics and Fittings	\$ 900
Samplers	3 - In-Line	\$ 300
Total Estimated Cost		\$5,800

DEWATERING UNIT

Equipment	Equipment Size/Type	Cost Estimate
Centrifuge	Batch Sludge Dewatering Unit	\$25,000
Flow Meter	Turbine w/ Electronics and Fittings	\$ 900
Sampler	In-Line	\$ 100
Total Estimated Cost		\$26,000

PYROMETALLURGICAL SMELTING UNIT TESTS

Unit Operations	Cost Estimate
Mixing Unit	\$ 100,000
Brick Making Unit	
Curing Unit	
Cupola	
Off-gas System	
	\$ 100,000

ELECTRICITY COSTS

Sludge Dewatering Unit Options

Option	Equipment	Electricity/day (kilowatt-hrs/day)	Total Elect./day (kilowatt-hrs/day)	Cost/Day (\$)
Froth Flotation Unit	2 Pumps	0.8	901	\$90.10
	Mixer	900		
Centrifuge Dewatering Unit	Centrifuge	540	540	\$54.00
	Feed Pump	0.4		
Settling Unit		No Power Required	0	\$0

Oxidation Unit Options

Option	Equipment	Electricity/day (kilowatt-hours/day)	Total Elect./day (kilowatt-hours/day)	Cost/Day (\$)
Electro- oxidation Unit	3 Pumps	1.2	221.6	\$22.16
	Small Mixer	4.5		
	Tank Mixer	17.9		
	Rectifier	162		
	Blower	36		
H ₂ O ₂ Oxidation Unit	2 Pumps	0.8	18.7	\$1.87
	Tank Mixer	17.9		

Oil/Water/Sludge Separation Unit

Equipment	Electricity/day (kilowatt-hours/day)	Total Elect./day (kilowatt-hours/day)	Cost/Day (\$)
Pump	0.4	4.9	\$0.49
Air Compressor	4.5		

Final Dewatering Unit

Equipment	Electricity/day (kilowatt-hours/day)	Total Elect./day (kilowatt-hours/day)	Cost/Day (\$)
Centrifuge	107	107	\$10.7

CHEMICAL COSTS

Chemical	Price	Amount Used/day	Cost/day
MIBC	\$1.00/pound	1 pound/day	\$ 1
NaCl	\$0.50/pound	78 pound/day	\$ 39
H ₂ O ₂	\$4.50/gallon	3 gallon/hour	\$324

OPERATION AND MAINTENANCE ESTIMATE CALCULATIONS

ESTIMATED MAINTENANCE AND OPERATION LABOR HOURS

Process	Operation hours	PM Equipment	PM Instrument	PM Electrodes	Total Hours
H ₂ O ₂	2700	100	100		2900
Electrooxide	4400	100	100	100	4700

For H₂O₂, estimates are 2.5 hours per shift for process control time, so for 3 shifts per day and 365 days a year, operator hours will be 2737.5 or rounded to 2700 hours. Preventive maintenance (PM) on the equipment is estimated at 1 day per motorized equipment or 10 times 1 equals 10 days or 80 hours or rounded to 100 hours per year. Preventive maintenance (PM) or calibration of instruments is estimated at 2 days per instrument per day; 7 times 2 equals 14 days or 112 hours or rounded to 100 hours.

For the electrolytic oxidation process, 4 hours are estimated per shift for process control time; operator hours will be 4380 hours per year, rounded to 4400 hours per year. PM on the equipment is estimated at 1 day per motorized equipment or 12 times 1 equals 12 days or 96 hours or rounded to 100 hours. PM or calibration of instruments is estimated at 2 days per instrument or 9 times 2 equals 18 days or 144 hours or rounded to 100 hours. PM for electrodes is estimated at two weeks or 10 days per year or 80 hours or rounded to 100 hours.

Processes with the concentration by centrifuge there will require an additional 8 hours for PM on the equipment. Also, there will be no additional PM or calibration for instruments.

Processes with the concentration by froth flotation will be resume an additional 32 hours for PM on the equipment. Also, there will be no additional PM or calibration for instruments.

For processes with concentration by settling, there will be no additional hours for PM for equipment and for instruments. This is because the feed tank will be considered as the concentration tank.

Automation of the control process can further minimize the operation time by the operator. The estimation for automation will have to be deferred until after the process parameter testing and process control system design.

Because of round off, the additional PM by the different concentration unit will not make any significant difference in the estimate.

ESTIMATED MAINTENANCE AND OPERATION MATERIAL COSTS

Process	PM Cost of Equipment	PM Cost of Instrument	PM Cost of Electrodes	Total Dollars
H ₂ O ₂	200	280	N/A	480
Electrolytic Oxidation	240	330	10,000	10,570

For H₂O₂, the PM cost for materials for equipment is estimated at \$20 for each unit for seals and lubricant for a total of \$200 for 10 units. The PM cost for materials for instruments is estimated at replacement parts for paddle wheel flow meters at \$33 or rounded to \$40 for seven flow meters or \$280.

For electrolytic oxidation, the PM cost for materials for equipments is estimated at 12 units for a total of \$240. The PM cost for materials for instruments is estimated at seven flow meters or \$280, and \$50 for gas monitor parts or a total of \$330. The electrodes are estimated to be replaced yearly at a cost of \$10,000.

For the concentration by settling, there is no addition material cost.

For the concentration by centrifuge, there is an additional \$20 material cost for belts, lubrication, and seals.

For the concentration by froth flotation, there is an additional \$80 material cost for belts, etc. for all four cells.